**ISTANBUL TECHNICAL UNIVERSITY ★ INSTITUTE OF SCIENCE AND TECHNOLOGY**

# THE PREPARATION OF ABC TYPE MIKTOARM STAR TERPOLYMER BY COMBINING OF DIELS-ALDER REACTION, ATOM TRANSFER RADICAL AND STABLE FREE RADICAL POLYMERIZATION ROUTES

**M. Sc. Thesis by**

**Figen KARATAŞ**

**Department : Polymer Science and Technology**

**Programme: Polymer Science and Technology**

**FEBRUARY 2006**

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**(515041020)**

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**Prof.Dr. Ömer ZAİM (T.Ü.)**

**FEBRUARY 2006**

**İSTANBUL TEKNİK ÜNİVERSİTESİ ★ FEN BİLİMLERİ ENSTİTÜSÜ**

# ABC TİP FARKLI KOLLU YILDIZ POLİMERİN DİELS-ALDER REAKSİYONU, ATOM TRANSFER RADİKAL VE KARARLI SERBEST RADİKAL POLİMERİZASYON YÖNTEMLERİ İLE HAZIRLANMASI

**YÜKSEK LİSANS TEZİ**

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**Tezin Enstitüye Verildiği Tarih : 19 Aralık 2005**

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**Prof.Dr. Ömer ZAİM(T.Ü.)**

**ŞUBAT 2006**

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**LIST of SYMBOLS**

| | |
|---|---|
| **ATRP** | **:** Atom Transfer Radical Polymerization |
| **SFRP** | **:** Stable Free Radical Polymerization |
| **RAFT** | **:** Reversible Addition-Fragmentation Chain Transfer Polymerization |
| **St** | **:** Styrene |
| ***t*BA** | **:** *Tert*-butyl acrylate |
| **LFRP** | **:** Living Free Radical Polymerization |
| **TEMPO** | **:** 2, 2, 6, 6- Tetramethylpiperidinoxy |
| $\mathbf{M_t^n}$ | **:** Transition metal |
| **L** | **:** Ligand |
| **I, M** | **:** Initiator and monomer respectively |
| $\boldsymbol{M_w/M_n}$ | **:** The Molecular Weight Distribution |
| $\mathbf{k_a}$ | **:** Rate constant of activation |
| $\mathbf{k_d}$ | **:** Rate constant of deactivation |
| $\mathbf{k_p}$ | **:** Rate constant of propagation |
| **DVB** | **:** Divinylbenzene |
| **THF** | **:** Tetrahydrofuran |
| **DMAP** | **:** 4-dimethylaminopyridine |
| **DCC** | **:** *N*,*N*-dicyclohexylcarbodiimide |
| **BPO** | **:** Benzoyl peroxide |
| **DPTS** | **:** 4-dimethylamino pyridinium-4-toluene sulfonate |
| **PMDETA** | **:** $N,N,N',N'',N''$ - pentamethyldiethylenetriamine |
| **GPC** | **:** Gel Permeation Chromotography |
| **NMR** | **:** Nuclear Magnetic Resonance Spectroscopy |
| **LUMO** | **:** Lowest Unoccupied Molecular Orbital |
| **HOMO** | **:** Highest Occupied Molecular Orbital |
| **DA** | **:** Diels-Alder Reaction |
| **PEG** | **:** Poly (ethylene glycole) |
| **UV** | **:** Ultra Violet Spectrophotometer |

**ABC TİP FARKLI KOLLU YILDIZ POLİMERİN DİELS-ALDER REAKSİYONU, ATOM TRANSFER RADİKAL VE KARARLI SERBEST RADİKAL POLİMERİZASYON YÖNTEMLERİ İLE HAZIRLANMASI**

## ÖZET


Yıldız polimerler araştırmalarda üç boyutlu ve çok dallanmış yapılarından dolayı yıllardır ilgi çekmektedirler. Yıldız polimerlerin sentezi genellikle yaşayan polimerizasyon yöntemiyle gerçekleştirilmektedir. Kontrollü/ "Yaşayan" Polimerizasyon yöntemlerinin iyi tanımlanmış ve kompleks yapılı polimerlerin sentezinde birçok açıdan faydalar sağladığı bilinmektedir. Kontrollü/ "Yaşayan" Radikal Polimerizasyon yöntemlerinin arasında Atom Transfer Radikal Polimerizasyonu (ATRP) ve Kararlı Serbest Radikal Polimerizasyonu (SFRP) özel blok kopolimerler ve yıldız polimerler gibi kompleks yapılı polimerlerin sentezinde en etkili yöntemlerdir.

ATRP ve SFRP gibi kontrollü polimerizasyon tekniklerinin bir avantajı da elde edilen polimerin molekül ağırlığının ve zincir uç grubu fonksiyonalitesinin kontrol edilebilir olmasıdır. Bu teknikler sayesinde polimer uç gruplarına çok çeşitli fonksiyonellikler kazandırılabilir ki bu da herhangi bir transformasyon reaksiyonu gerektirmeden iyi tanımlı polimerlerin eldesine izin verir.

Dields-Alder reaksiyonu son yıllarda organik sentez için en önemli sentetik metodlardan biridir. Bu reaksiyon genellikle bir dien ile dienofilin çiftleşmesini içerir. Dields-Alder reaksiyonu çoğunlukla çift bağ ve fonksiyonel grup için koruma metodu olarak kullanılır.

ABC tip miktoarm yıldız terpolimer, Diels-Alder reaksiyonu (DA), kararlı serbest radikal polimerizasyonu (SFRP) ve atom transfer radikal polimerizasyonunun (ATRP) birleşimi vasıtasıyla iç çekirdek ve dış çekirdek metotları kullanılarak hazırlanmıştır. İlk olarak, Diels-Alder reaksiyonunda, başlangıç maddesi poli(etilen glikol)-maleimide (PEG-maleimide) SFRP ve ATRP için uygun fonksiyonel grupları içeren Diels-Alder katılma ürününü ,15, elde etmek üzere süksinik asit antrasen-9-ylmetil ester 3-(2-bromo-2-metil-propiyoniloxy)-2-metil-2-[2-fenil-2-(2,2,6,6-tetrametil piperidin-1-yloxy)-etoksi-carbonil]-propil ester ,8, ile reaksiyona sokuldu. İkinci olarak, öncelikli olarak elde edilen 15, 125 $^{o}$C de stirenin SFRP'si için makrobaşlatıcı olarak kullanıldı. Üçüncü olarak, çelirdekte brom fonksiyonlu PEG-polistiren (PEG-PSt), başlangıç maddesi, CuBr ve PMDETA varlığında 80 $^{o}$C de kontrollü molekül ağırlıklı ve düşük polidispersiteli ABC tip miktoarm yıldız terpolimeri vermek için tersiyer butil akrilat'ın ATRP si için makrobaşlatıcı olarak kullanıldı.

## 1. INTRODUCTION

Miktoarm star polymers have been synthesized on the basis of two general strategies [1, 2]. The first involves the use of living anionic polymers to be consecutively reacted with an appropriate multifunctional core (chlorosilane compound) in a consecutive polymer reaction. The second is the reaction of the active chain with divinylbenzene (DVB). In this route, living polymer (derived from anionic polymerization) is added to DVB affording to the formation of a star polymer with active anionic sites on the polymer core. Subsequent anionic polymerization of another monomer results in the miktoarm star polymer. The ionic polymerizations (anionic or cationic) were the only living systems available until recently. These systems give the polymers with the controlled molecular weight, well-defined chain ends and low polydispersity. In recent years, the use of the controlled/living radical polymerization (CRP) techniques in the synthesis of complex macromolecules has fast increased because of the variety of applicable monomers and more tolerant experimental conditions than the living polymerization routes require. The stable free radical polymerization [3] (SFRP) based on the use of stable nitroxide free radicals and $M_t^n$/Ligand catalyst mediated atom transfer radical polymerization [4-6] (ATRP) are versatile methods for the controlled radical polymerizations. Although a remarkable progress in all controlled/living radical polymerization processes, there are still some disadvantages such as removal of transition metal catalyst for the purification of polymer (particularly in ATRP), and relatively higher polydispersities. In addition, living ring opening polymerization (ROP) technique has found a wide application in the polymerization of lactones and lactides [7]. Recently, the combinations of different controlled/living polymerization techniques have been used to prepare miktoarm star polymers. By using ATRP/ ROP techniques, the syntheses of $A_3B_3$ type [8], poly(methyl methacrylate)$_3$-poly(caprolactone)$_3$, $(PMMA)_3$-$(PCL)_3$, $AB_2$ type [9], (PCL)-(P*t*BA)$_2$ or (PCL)-$(PMMA)_2$ miktoarm star polymers were carried out.

The preparation of $AB_2$ type [10], polystyrene-(P*t*BA)$_2$, (PSt) (P*t*BA)$_2$, miktoarm star- and –block copolymers, $AB_2C_2$ type [10], (PSt)-(P*t*BA)$_2$ (PMMA)$_2$, and $A_3B_3$ type [11], (PSt)$_3$-(PMMA)$_3$ via combinations of the controlled free radical polymerizations: SFRP/ ATRP, ABC type miktoarm star polymers consisting of poly(tetrahydrofuran)(PTHF)-poly(dioxepane)-(PSt) [12] via combination of cationic ring opening polymerization (CROP)/ ATRP and (PCL)-(PSt)-(P*t*BA) [13] or (PCL)-(PSt)- (PMMA) [14] via combination of ROP/ SFRP/ ATRP have been reported by many groups.

The Diels-Alder reaction (DA), [4+2] system, generally consists of a coupling of a diene and a dienophile by intra- or intermolecular reaction [15]. Recently, DA reaction has attracted much attention based on the macromolecular chemistry particularly providing new materials [16-21].

The purpose of this work was to involve DA reaction for the preparation of ABC type miktoarm star terpolymer with poly(ethylene glycol) (PEG), PSt and P*t*BA arms. This aim was achieved by combining DA reaction of maleimide-end functionalized PEG (PEG-maleimide), SFRP of St and ATRP of *t*BA routes. Meanwhile, we focused on model DA reaction between 9-anthyrylmethyl 2-bromo-2-methyl propanoate and *N*-ethyl maleimide, and furthermore, investigated whether polymeric DA reaction proceed in high yield between maleimide end functionalized PEG (PEG-maleimide) and 9-anthyrylmethyl 2-bromo-2- methyl propanoate.

# 2. THEORETICAL PART

## 2.1. Controlled/ 'Living' Free Radical Polymerizations

The development of controlled/''living'' radical polymerization (CRP) is among the most important advances in the field of polymer science during the last ten years. CRP offers the possibility of synthesizing various homopolymers and copolymers with molecular weight predetermined by the ratio of consumed monomer to the introduced initiator, low polydispersities, controlled compositions, functionalities and chain topologies. Several methods allowing control of radical polymerization have been reported [22].

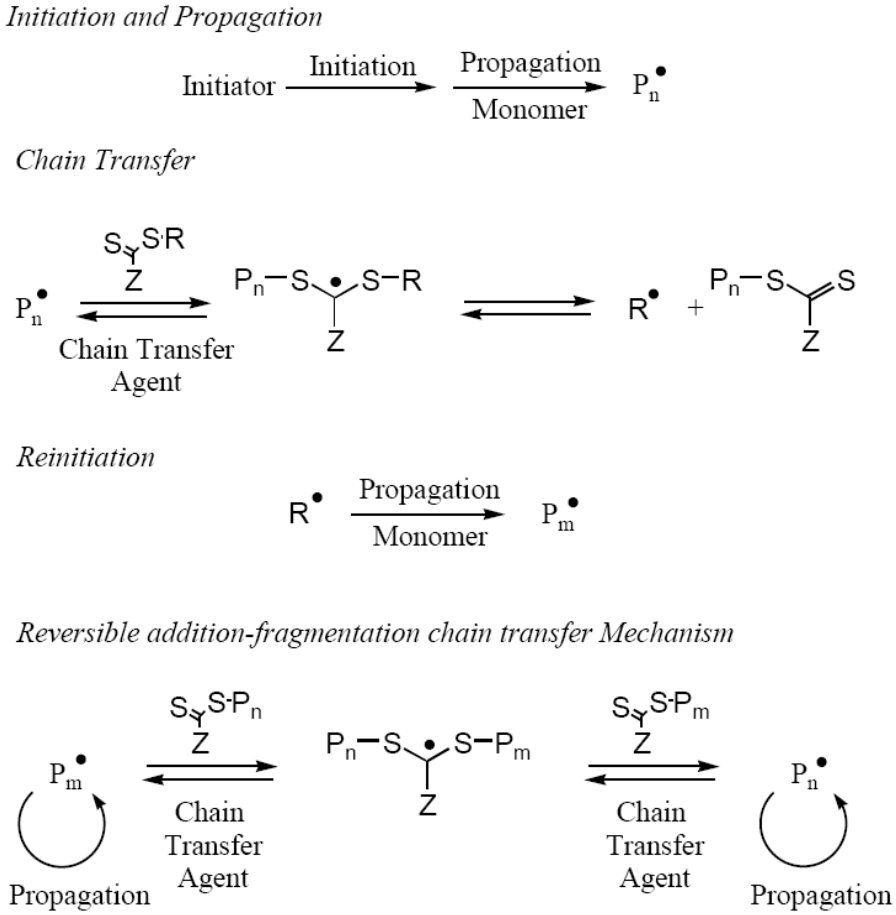
### 2.1.1. Iniferter

In 1982, Otsu et al. extended the idea of living polymerizations to free radical systems in the use of initiator-transfer-agent-terminators, or iniferters [23]. Such initiators act both as primary radicals to initiate polymerization and as radical chain terminators consequently permitting a near linear increase of molar mass with time and percent conversion [24]. However, the similarities between living anionic systems and Otsu's iniferter reaction end there. The iniferter mechanism yields radicals that can initiate new chains throughout the course of the reaction. The iniferter systems also show significant loss of active end groups from the growing polymers. Consequently, these systems display relatively large polydispersities with a substantial amount of homopolymer being formed in conjunction with block copolymer [25].

### 2.1.2. Reversible Addition – Fragmentation Chain Transfer Reactions (RAFT)

Most recent report of a controlled/"living" free radical polymerization has been reported by Haddleton and co-workers as well as Thang et al. [26]. Reversible addition-fragmentation chain transfer (RAFT) is achieved by performing a free radical polymerization in the presence of dithio compounds, which act as efficient reversible addition-fragmentation chain transfer agents (sheme 2.1). Much like the

first two routes, the rapid switching mechanism between dormant and active chain ends affords living polymerization character.



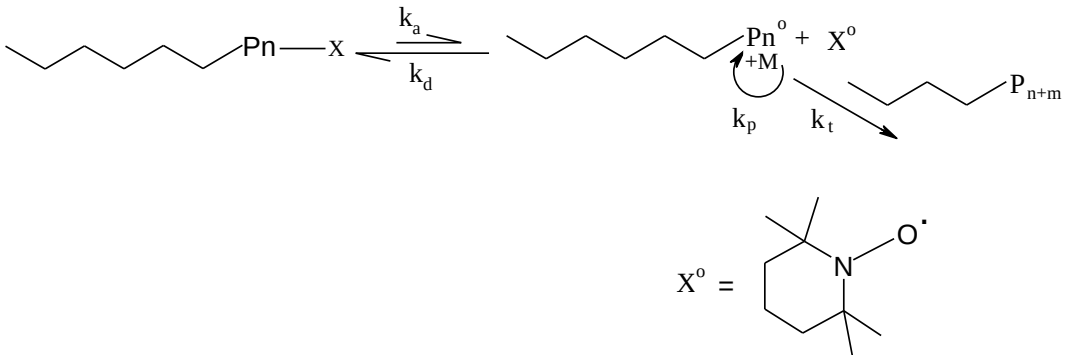

Scheme 2.1. RAFT mechanism

### 2.1.3. Nitroxide-Mediated Living Radical Polymerizations (NMP)

Nitroxide–mediated living free radical polymerization (NMP) belongs to a much larger family of processes called stable free radical polymerizations. In this type of process, the propagating species (Pn°) reacts with a stable radical (X°) as seen in Scheme (2.2). The resulting dormant species (Pn-X) can then reversibly cleave to regenerate the free radicals once again. Once Pn° forms it can then react with a monomer, M, and propagate further. The most commonly used stable radicals have been nitroxides, especially 2,2,6,6-tetramethylpiperidinoxy (TEMPO).

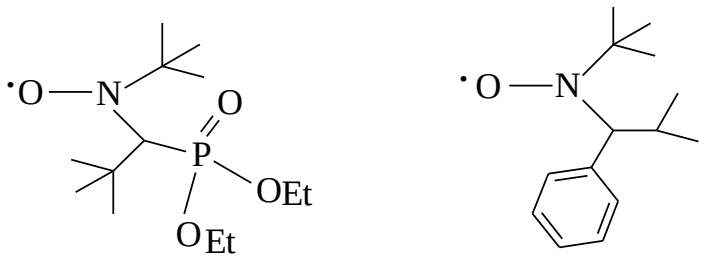
Although NMP is one of the simplest methods of living free radical polymerization (LFRP), it has many disadvantages. Many monomers will not polymerize because of the stability of the dormant alkoxyamine that forms. Also, since the reaction is

kinetically slow, high temperatures and bulk solutions are often required. Also, the alkoxyamine end groups are difficult to transform and require radical chemistry.




Scheme 2.2**.** The mechanism for nitroxide-mediated polymerization

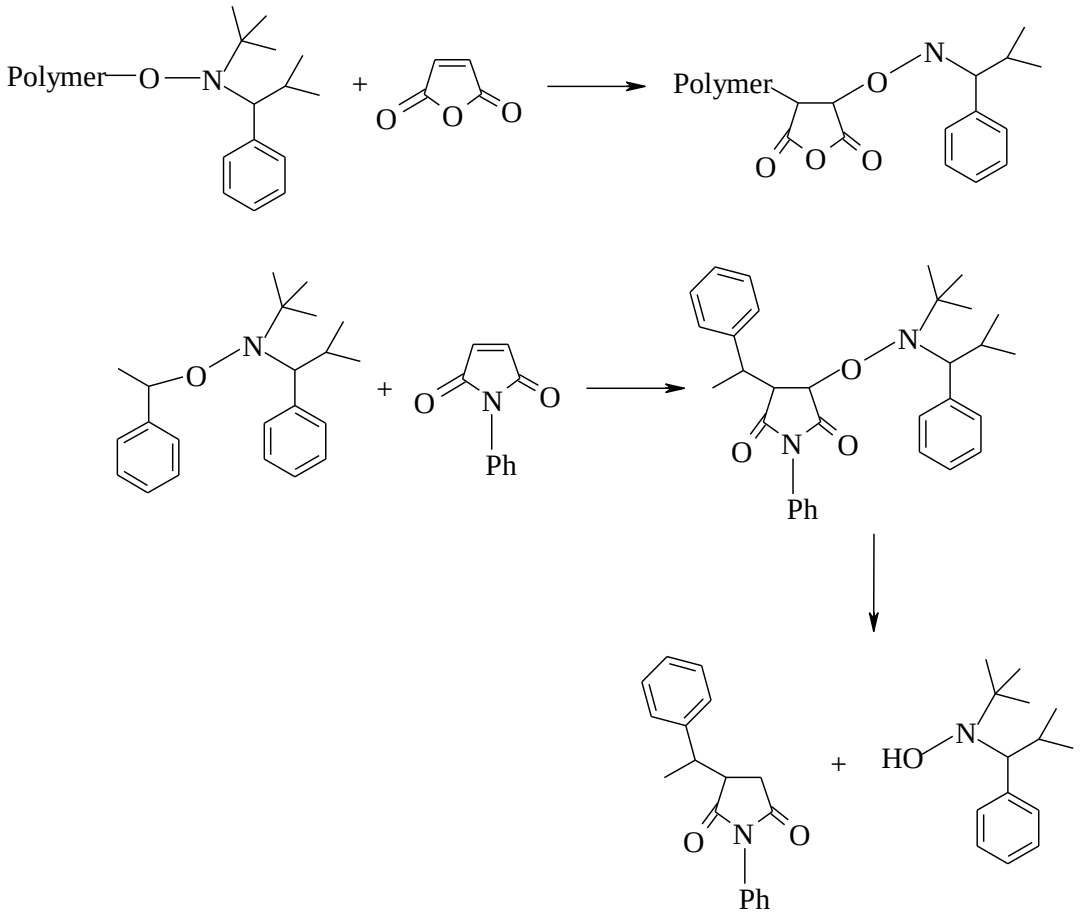
Recent work in NMP has revolved around the synthesis and evaluation of new nitroxide radicals, chain end functionalization, and the exploration of the synthesis of block, random, star, and graft copolymers. A review has recently been published which covers these topics in detail [27]. The most popular nitroxide used for NMP in the past has been TEMPO. However, TEMPO is limited in the range of monomers which are compatible to polymerize by NMP, mostly due to the stability of the radical. Hawker et. al. recently discovered that by replacing the α-tertiary carbon atom with a secondary carbon atom, the stability of the nitroxide radical decreased which lead to an increased effectiveness in polymerization for many monomers in which TEMPO was uneffective [28] (scheme 2.3). While TEMPO and TEMPO derivatives are only useful for styrene polymerizations, the new derivatives permit the polymerization of acrylates, acrylamides, 1,3-dienes, and acrylonitrile based monomers with very accurate control of molecular weights and low polydispersities. Another family of nitroxides that have shown to have the same success are phosphonate derivatives designed by Gnanou et.al. [29].




Scheme 2.3. TEMPO derivatives

The chain end functionalization of polymers synthesized by NMP is a significant problem because dormant chains containing alkoxyamines can regenerate terminal

radicals which can depolymerize at high temperatures. A very interesting chain end functionalization process has also been discovered by Hawker et. al. which involves the controlled monoaddition of maleic anhydride or maleimide derivatives to the alkoxyamine chain end [30]. The alkoxyamine can then be easily eliminated and other functional groups can be introduced. This process relies on the resistance of maleic anhydride or maleimide derivatives to homopolymerize and the ability of the precurser to reform the olefin by elimination of the hydroxylamine (scheme 2.4).




Scheme 2.4. Chain end functionalization process.

NMP is an excellent method for synthesizing diverse and well defined macromolecular structures. Block copolymers can be synthesized in many varying ways. Amphiphilic materials were synthesized by Frechet et al by first reacting a polyether with chlorinated alkoxyamine derivative to form a macroinitiator [31]. The macroinitiator then underwent polymerization with styrene to produce amphiphillic block copolymer with very low polydispersities and accurately controlled molecular weights. Other block copolymerizations have combined NMP with other polymerization methods such as transition metal mediated [32], anionic [33], ring

opening [34], or even radical [35]. Also, block copolymers can be constructed by the polymerization of one monomer followed by another. This can be realized due to the living nature of the polymerization which allows the chain ends at 100% conversion to be reactive

### 2.1.4. Atom Transfer Radical Polymerization (ATRP)

ATRP is one of the most versatile living/controlled radical polymerization techniques that allow for the preparation of polymeric materials with well-defined molecular weights, compositions, functionalities and architectures [36]. The basis of this technique is the reversible transfer of a halogen atom from a monomeric or polymeric alkyl halide (R–X) to a transition metal complex ($LM_t^n$), generating an organic radical and a transition metal complex ($LMn_t^{n+1}X$) with a higher oxidation state (scheme 2.5) [37]. To establish the equilibrium between $LM_t^n$ and $LMn_t^{n+1}X$ strongly shifted toward the $LM_t^n$ complex, many factors should be taken into consideration, involving the monomer, initiator with a transferable (pseudo) halogen, catalyst (composed of a transition metal species with any suitable ligand), solvent and temperature [38].

$$R-X + LM_t^n \rightleftharpoons R^{\bullet} + LM_t^{n+1}X$$

Scheme 2.5. Redox dynamic equilibrium reaction (M.monomer, $M_t$.metal)

#### 2.1.4.1. Typical features of ATRP:

A successful ATRP process should meet several requirements [39] :

1) It should consume the initiator at the early stages of polymerization and generate propagating chains leading to polymers with degrees of polymerization (DP) predetermined by the ratio of the concentrations of converted monomer (M) to the introduced initiator (I) ($DP = \Delta[M] / [I]_o$).

2) The number of monomer molecules added during one activation step should be small, resulting in polymers with low polydispersities.

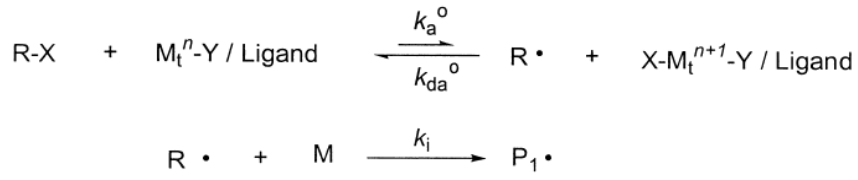
3) Finally, the contribution of chain-breaking reactions (transfer and termination) should be negligible so as to yield polymers with high degrees of end functionalities and allow the synthesis of block copolymers.

### 2.1.4.2. Elementary Reactions

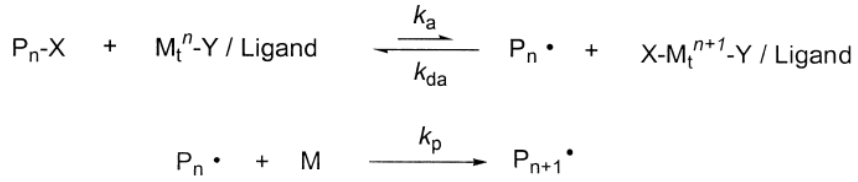
Similar to RP, the elementary reactions in ATRP consist of initiation, propagation, transfer and termination (scheme 2.6). However, succesful ATRP behaves quite differently than RP. Initiation in ATRP must be fast and completed at low monomer conversion. Termination should be suppressed and usually much less than 10% of all chains terminate. Rate and concentration of propagating radicals is established by equilibration between activation and deactivation steps and not via steady state as in RP in which rates of initiation and termination are essentially equal. Transfer in most cases may be neglected because polymers with relatively low molecular weights are targeted.

For a well-controlled ATRP, initiation should be fast and quantitative. The apparent initiation rate constant ($k_i^{app} = k_i K_o$, where $k_i$ and $K_o$ refer to the absolute rate constant of addition of the initiating radical to the aklene and the atom transfer equilibrium constant for the initiating species, respectively) should be at least comparable to the apparent propagation rate constant ($k_p^{app} = k_p K_{eq}$, where $k_p$ and $K_{eq}$ refer to the absolute rate constant of propagation and the atom transfer equilibrium constant for the propagating species, respectively). If $k_i^{app} << k_p^{app}$, polymers with higher molecular weights than the theoretical values and higher polydispersities will be obtained. This behavior is based on the assumptionthat the system is equilibrated or there was deactivator added initially. The situation is more complex when the amount of the deactivator is small and the rate determining step of initiation is only activation. If initiation is too fast and a lot of radicals are generated during the initiation step, irreversible radical termination will reduce the initiator efficiency and slow down the polymerization. A general guideline for choosing a suitable ATRP initiator is that the initiator should have a chemical structure similar to the dormant polymer species.

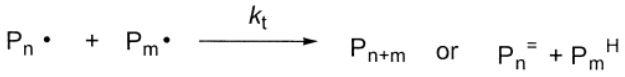
**Initiation**




**Propagation**




**Termination**




Scheme 2.6. Elementary reactions in ATRP

These rules also apply to cross-propagation step in block copolymerization. We refer to reactivities of monomer in ATRP in terms of $k_p^{app}$, which does not scale with the true $k_p$ values. Efficient crossing in block copolymerization requires $k_{cross}^{app} > k_p^{app}$, unless halogen Exchange is employed [40].

Polymer chains propagete by adding new monomer units to the growing chain ends. To obtain well-defined polymers with low polydispersities, it is crucial to rapidly deactivate the growing chains to form dormant species. Termination occurs through combination or disproportionation pathways and is most significant at the beginning of the polymerization. After a sufficient amount of the higher oxidation state metal complex has been built up by the irreversible termination reaction, the persistent radical effect predominates and radical termination is minimized [41]. It has been proposed that termination rate coefficients are chain length dependent and decrease during the polymerization to result in a steady rate of polymerization [42]. This helps to form well-defined polymers at higher conversions. However, when the monomer concentration becomes very low, propagation slows down but termination and other side reactions may stil ocur with the usual rate. Thus, there is a certain window of concentrations and conversions where the polymerization is well controlled.

In ATRP there might be additional side reactions, not present in RP. They may include loss of activity by OSET, heterolytic cleavage of R-X bond, loss of HX at elevated temperatures in polar solvents, nucleophilic displacement of X by basic solvents and additives (or monomers), supplementary transfer with ligands and complexes and some others. Proper choice of reaction conditions and understanding of the physical organic chemistry associated with those side reactions may reduce thir contribution.

ATRP is a complex process based on several elemantary reactions. Success depends on controlling all of them as well as on controlling the concentrations and reactivities of the involved species. The rate constants of radical propagation are systematically being evaluated by pulsed laser polymerization techniques. The rate constants of termination are less accessible, as they depend on the chain length and the viscosity of the medium. As discussed before, in ATRP perhaps most important are the rate constants for the activation and deactivation steps. They depend on the structure of monomer (i.e. the radical and the dormant species), on the halogen and, obviously, on the transition metal complexes. The values of the rate constants of some of these reactions have been reported for the polymeric species and some for the model systems, which mimic the structure of the dormant/active species [43].

#### 2.1.4.3. Monomers

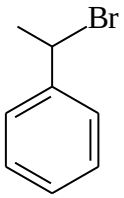
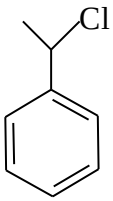
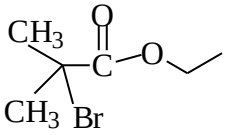
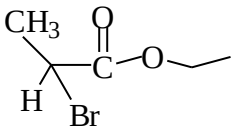
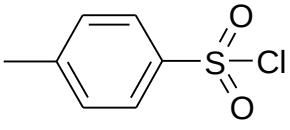
A variety of monomers have been succesfully polymerized using ATRP. Typical monomers include styrenes, (meth) acrylates, (meth) acrylamides, and acrylonitrile, which contain substituents that can stabilize the propagating radicals. Even under the same conditions using the same catalyst, each monomer has its own unique atom transfer equilibrium constant for its active and dormant species. In the absence of any side reactions other than radical termination by coupling or disproportionation, the magnitude of the equilibrium constant *($K_{eq}=k_{act}/k_{deact}$)* determines the polymerization rate.

#### 2.1.4.4. Initiators

The main role of the initiator is to determine the number of growing polymer chains. Two parameters are important for a succesful ATRP initiating system. First, initiation should be fast in comparison with propagation. Second, the probability of the side reactions should be minimized.

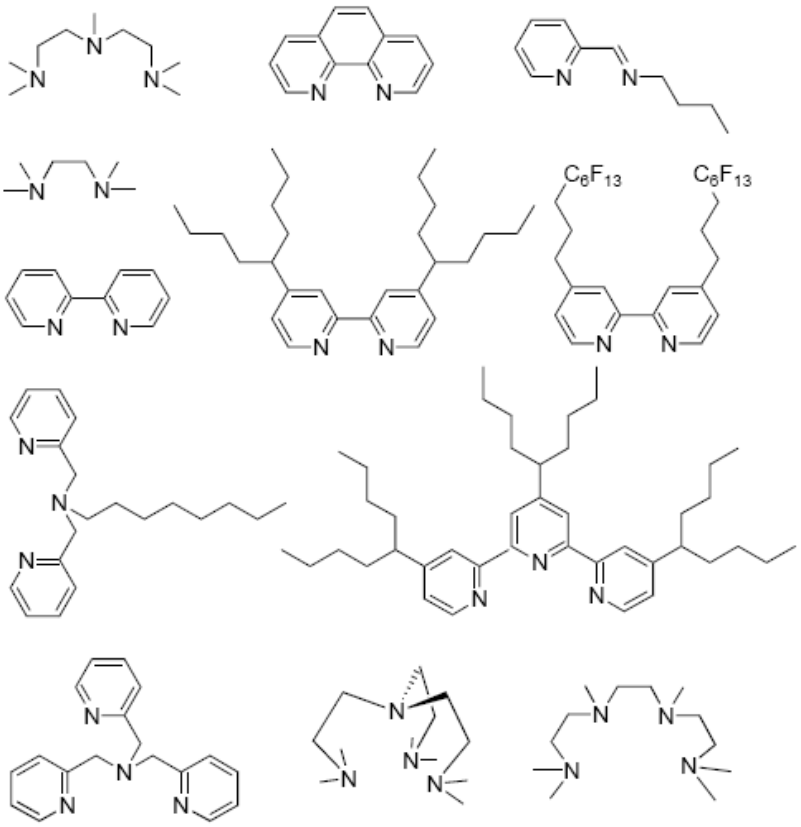
In ATRP, alkylhalides (RX) are typically used as initiator and the rate of polymerization is first order with respect to the concentration of RX.To obtain well-defined polymers with narrow molecular weight distributions, the halide group, X, must rapidly and selectively migrate between the growing chain and the transition metal complex. When X is either bromine or chlorine, the molecular weight control is the best. Flourine is not used because the C-F bond is too strong to undergo homolytic cleavage.

Table 2.1. The most frequently used initiator types in ATRP systems

| Initiator | Monomer |
|---|---|
|  1-Bromo-1-phenyl ethane | Styrene |
|  1-Chloro-1-phenyl ethane | Styrene |
|  Ethyl-2-bromo isobutyrate | Methyl methacrylate |
|  Ethyl-2-bromo propionate | Methylacrylate and other acrylates |
|  p-toluene sulphonyl chloride | Methyl methacrylate |

### 2.1.4.5. Ligands and Metals

The main role of the ligand in ATRP is to solubilize the transition metal salt in the organic media and to adjust the redox potential of the metal center for the atom transfer. There are several guidelines for an efficient ATRP catalyst. First fast and quantitative initiation ensures that all the polymer chains start to grow simultaneously. Second, the equilibrium between the alkylhalide and the transition metal is strongly shifted toward the dormant species side. This equilibrium position will render most of the growing polymer chains dormant and produce a low radical concentration. As a result, the contribution of radical termination reactions to the overall polymerization is minimized. Third fast deactivation of the active radicals by halogen transfer ensures that all polymer chains are growing at approximately the same rate, leading to a narrow molecular weight distribution. Fourth relatively fast activation of the dormant polymer chains provides a reasonable polymerization rate. Fifth, there should be no side reactions such as $\beta$-H abstraction or reduction/oxidation of the radicals. Some ligands used successfully in ATRP are shown in scheme (2.7).




Scheme 2.7. Some ligands used successfully in ATRP.

The most widely used ligands for ATRP systems are the derivatives of 2,2-bipyridine and nitrogen based ligands such as *N*,*N*,*N*',*N*'',*N*''-pentamethyldiethylenetriamine (PMDETA), tetramethylethylenediamine (TMEDA), 1,14,7,10,10-hexamethyltriethylenetetraamine(HMTETA), tris[2-(dimethylamino) ethyl]amine (Me-TREN) and alkylpyridylmethanimines are also used.

Catalyst is the most important component of ATRP. It is the key to ATRP since it determines the position of the atom transfer equilibrium and the dynamics of exchange between the dormant and active species. There are several prerequisities for an efficient transition metal catalyst. First, the metal center must have at least two readily accesible oxidation states separated by one electron. Second the metal center should have reasonable affinity toward a halogen. Third the coordination sphere around the metal should be expandable upon oxidation to selectively accomodate a (pseudo)-halogen. Fourth the ligand should complex the metal relatively strongly.

The most important catalysts used in ATRP are; Cu(I)Cl, Cu(I)Br, $NiBr_2(PPh_3)_2$, $FeCl_2(PPh_3)_2$, $RuCl_2(PPh_3)_3$/ $Al(OR)_3$.

#### 2.1.4.6.Media/solvents

ATRP can be carried out either in bulk, in solution or in a heterogeneous system (e.g., emulsion, suspension). Various solvents such as benzene, toluene, anisole, diphenyl ether, ethyl acetate, acetone, dimethyl formamide (DMF), ethylene carbonate, alcohol, water, carbon dioxide and many others have been used for different monomers. A solvent is sometimes necessary especially when the obtained polymer is insoluble in its monomer [38].

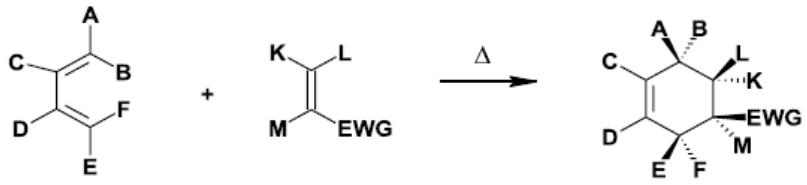
## 2.2. Diels-Alder Reactions

### 2.2.1. General Features

The Diels-Alder reaction is a concerted [4π+2π] cycloaddition reaction of a conjugated diene and a dienophile. This reaction belongs to the larger class of pericyclic reactions, and provides several pathways towards the simultaneous construction of substituted cyclohexenes with a high degree of regioselectivity, diastereoselectivity and enantioselectivity [44].

Many different versions of the Diels -Alder reaction were elaborated, including intramolecular [4+2] cycloadditions, hetero Diels-Alder reactions, pressure-accelerated Diels-Alder reactions, and Lewis acid accelerated Diels-Alder reactions [45].

The original version of the Diels-Alder reaction (scheme 2.8) joins together a wide variety of conjugated dienes and alkenes with electron withdrawing groups (the dienophiles), to produce a cyclohexene ring in which practically all six carbon atoms can be substituted as desired. The reaction may be executed under relatively simple reaction conditions by heating together the two components, diene and dienophile, in non-polar solvents, followed by evaporation which leads usually to high yields of the product(s). The reaction is disciplined by the Woodward- Hoffmann rules [46] as a $[_{\pi}4_{s}+_{\pi}2_{s}]$ cycloaddition occurring in a concerted but probably not symmetrically synchronous fashion, thus leading to highly predictable product structures in which two new carbon-carbon sigma bonds are formed in a stereospecific manner with the creation of up to four new stereogenic centres. The classical empirical rules have now found strong theoretical basis in the Woodward- Hoffmann rules, with regards to regiochemistry ("*ortho*" and "*para*" orientations) and stereochemistry (*endo* transition state kinetically favoured over the *exo* transition state in most of the reactions). The practising synthetic organic chemist will certainly be well aware of the kinds of dienes and dienophiles that may be combined successfully, and by way of simple frontier orbital theory be perfectly capable of predicting the major (or unique) product to be expected from the reaction. The reverse process of retrosynthetic analysis is also well established for transforming cyclohexene/ cyclohexane containing structures into appropriate diene dienophile combinations.

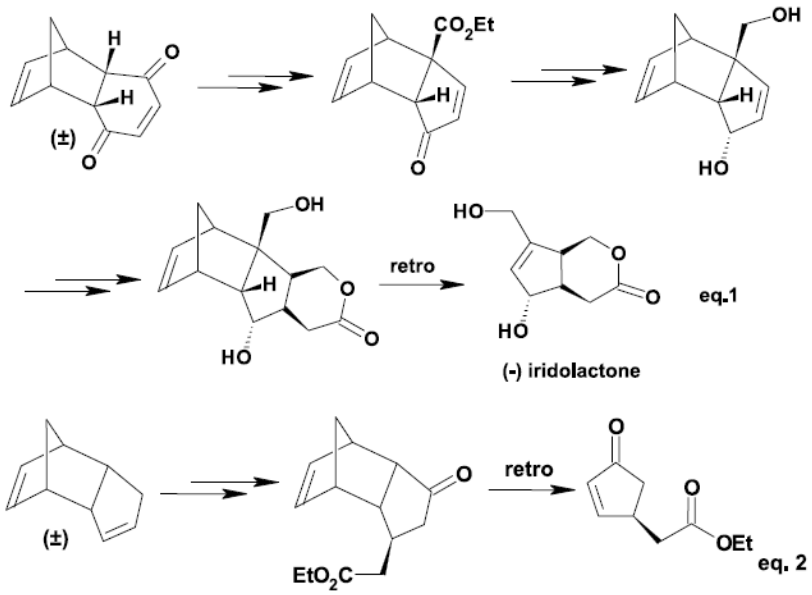



A — F and K — M: substituents; EWG: electron withdrawing group

Scheme 2.8. The original version of the Diels-Alder reaction

The Diels-Alder reaction has now become an important research area for theoretical chemists, with regard to the finer details of the transition state and the energetics of the process, and with special concern for entropy and activation energies.

A final introductory point illustrates a powerful synthetic strategy of Diels-Alder chemistry as a protecting group and temporary scaffold (or template), for the manipulation of the sensitive multiple functionalities of diene or dienophile types. In this approach the sensitive diene or dienophile portions of the molecules are tied up with a convenient partner in a Diels-Alder reaction, the cycloadduct is then chemically modified in accordance with the synthetic plan and finally undergoes a retro Diels-Alder reaction to liberate the desired product. For example, the cycloaddition product of a reactive α,β-enone function with cyclopentadiene, can be submitted to the required chemo-, regio- and stereoselective reactions, dominated in part by the expected *endo*-cycloadduct structure, before retro Diels- Alder reaction unravels a much more complex product. Clearly the same synthetic sequence could not have been executed on the enone itself, with the desired efficiency and selectivity, as demonstrated for the transformation of *para*-benzoquinone into the monoterpene (-)-iridolactone (scheme 2.9 ; equation 1). In a similar vein the cyclopentadiene dimer itself (scheme 2.9 ; equation 2) can be suitably modified and then a retro Diels-Alder reaction furnishes a useful chiral cyclopentenone derivative, as a diene precursor for a further Diels-Alder cycloaddition. In both of these examples intermediates undergo kinetic enzymatic resolutions with lipases, thus producing enantiopure cyclopentene derivatives [47-49].

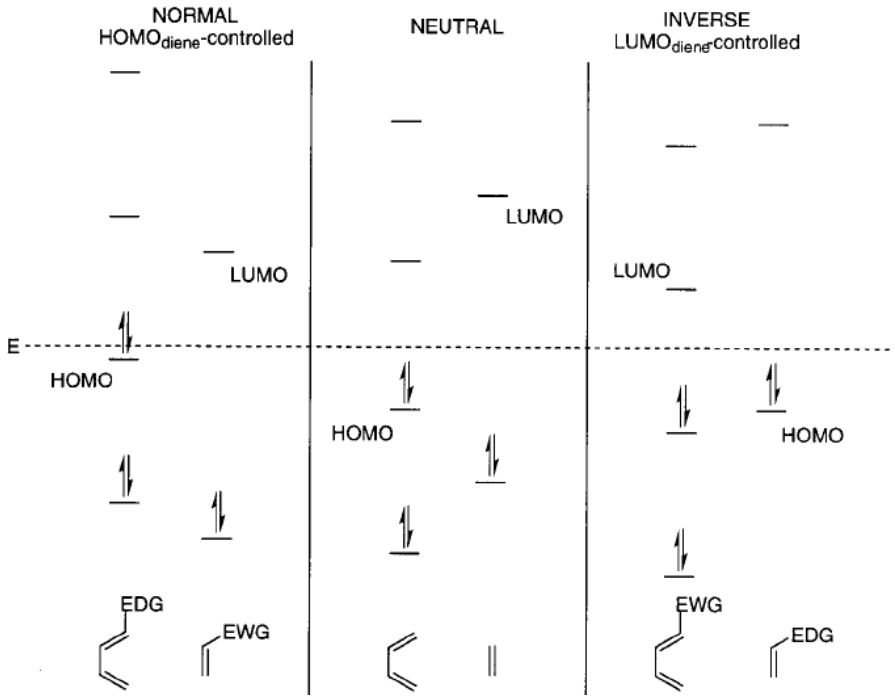



Scheme 2.9. Producing enantiopure cyclopentene derivatives.

### 2.2.2. Mechanistic aspects

A given Diels-Alder reaction may be described as conforming to one of three general $_{\pi}4_{s}+_{\pi}2_{s}$ cycloaddition types. These types are the 'normal' $HOMO_{diene}$-controlled reaction, the neutral reaction and the 'inverse electron demand' $LUMO_{diene}$-controlled Diels-Alder reaction. The cycloaddition type and corresponding reaction rate correlate with the magnitude of the smallest diene-dienophile HOMO-LUMO energy difference. Electronic and structural features of the reagents determine the size of this energy difference and consequently the nature of the reaction.

The most commonly utilized Diels-Alder type in organic synthesis is the $HOMO_{diene}$-controlled 'normal' type in which an electron-deficient dienophile is used (scheme 2.10) [50].




Scheme 2.10. The most commonly utilized Diels-Alder types.

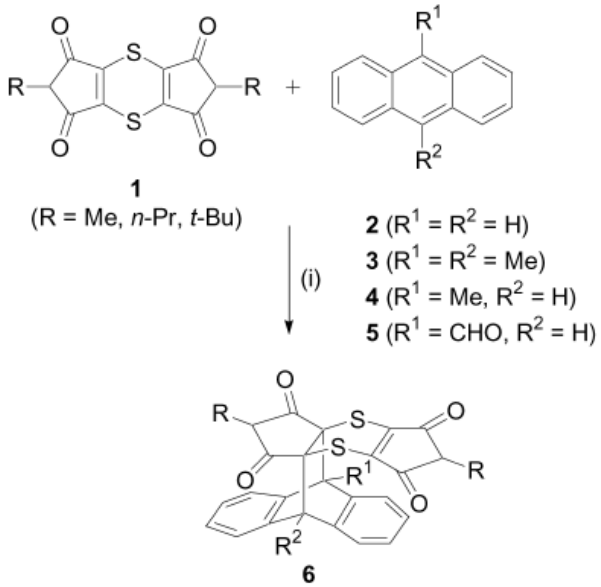
### 2.2.3 Mechanism of Diels–Alder Reactions with Anthracene

#### 2.2.3.1. Thermal Mechanism

The mechanism of the thermal [4+2] cycloaddition reaction of anthracene with a dienophile has been the source of much conjecture. The stereochemistry of the reaction involves exclusive cis addition of the dienophile to anthracene where the cis or trans stereochemistry of the dienophile is retained in the product. The retention of

stereochemistry has led many groups to postulate a concerted mechanism, where the new σ bonds are formed simultaneously either by direct addition, or via an intermediate charge–transfer complex or an electron donor–acceptor molecular complex. Another possibility is a two-step reaction mechanism where the reaction proceeds via a zwitterionic or diradical intermediate. For a two-step mechanism to occur with retention of stereochemistry, the second step of the reaction would have to be much faster than the rotation about the C–C σ bond of the intermediate formed in the first step.

Many studies have noted the production of a transient colour that disappears as the thermal Diels–Alder reaction proceeds. This has been attributed to the formation of a charge–transfer complex during the course of the reaction and seems, therefore, to provide evidence for a concerted mechanism. Studies carried out with 1,4-dithiins 1 and anthracene 2 and its derivatives 3–5 (scheme 2.11) have shown that the formation of the Diels–Alder adducts 6 can in fact occur either via a charge–transfer complex or by direct addition, depending on the properties of the anthracene derivative used .




Scheme 2.11. Reagents and conditions: (i) $C_6H_6$, Δ.

The first pathway proceeding via the formation of a charge– transfer complex was dominant when using anthracene 2 and the electron-rich derivatives 3 and 4. Evidence for charge–transfer complex formation came from the colour change seen during the course of the reaction. The formation, and subsequent disappearance of the charge– transfer complex was monitored using UV spectrophotometry observing

absorption bands in the region of 400 to 650 nm. The second pathway, by direct cycloaddition, was only available for the modestly electrondeficient anthracene derivative 5. The change in mechanism was accompanied by a decrease in the reaction rate. In terms of FMO theory, the rate trend paralleled the HOMO energy levels with charge–transfer complex formation only occurring when the HOMO–LUMO energy difference between diene and dienophile was small, whereas the direct cycloaddition mechanism occurred when this difference was much larger.

The effect of solvent on the rate of reaction has been studied by many groups. The electron-donating ability of the solvent has been shown to be an important factor that affects the rate of reaction. Electron-donating solvents increase solvation of the dienophile that can in turn decrease the reaction rate. Solvents that are electron accepting can, in some cases, increase the rate of reaction by stabilisation of the transition state, which can be regarded as being electron rich. Aromatic solvents produce large increases in reactivity with dienophiles that are capable of very strong charge–transfer interactions, while salt effects have been observed for reactions performed in water. However, in general, the influence of the solvent on the rate of reaction, independent of the system investigated, has been shown to be relatively small, rarely above a factor of ten. This can be seen as evidence for a concerted mechanism as solvent effects would be expected to be large if a stepwise mechanism was in operation due to solvent stabilisation/ destabilisation of zwitterionic or diradical intermediates. However, the use of highly-fluorinated solvents has been shown to have a dramatic effect on the rate of the Diels–Alder reaction of 9-hydroxymethylanthracene and N-ethylmaleimide. Additionally, changes in the solvent can also have an effect on the endo/exo selectivity of the Diels–Alder reaction by a complex combination of solvent solvophobicity, dipolarity and hydrogen bond-donating effects.

The rate of the Diels–Alder reaction of anthracene appears to be governed much more by temperature and substituent effects. As the Diels–Alder reaction of anthracene is an equilibrium process, changes in temperature have a decisive effect on the position of the equilibrium. Lower reaction temperatures coupled with an excess of dienophile can increase the forward reaction rate, whereas higher temperatures can actually favour the retro Diels–Alder reaction.

Substituent effects have been found to be much more complex, with either substituents on anthracene, substituents on the dienophile, or a combination of the two features to be considered. In general, the reactivity of anthracene can be increased by substitution with electron-donating groups in the 9 and 10 positions, whereas electron-withdrawing substituents have the opposite effect. However, in some cases, the steric effect of substituents can decrease the reaction rate by overriding any electronic effects. For example, substitution with the normally-electron-donating $Me_3Si$ group in the 9 position results in very little rate enhancement over anthracene, and disubstitution with $Me_3Si$ leads to a complete lack of reactivity. The relationship between electronic and steric effects has been shown to be complex, with sterically demanding groups often reacting faster than less bulky groups. It has been suggested that this effect is due to a release of the compression placed on bulky groups by the peri hydrogen atoms of anthracene with the change in hybridisation from $sp^2$ to $sp^3$ that occurs in the Diels–Alder reaction .

The dienophile in the Diels–Alder reaction may be considered to have Lewis acid character, accepting the π electrons from a donor (the diene). The main effect of substituents on the dienophile is to alter the electronic properties, thus changing its ability to accept π electrons. Therefore, electron-withdrawing substituents generally increase the reactivity of the dienophile by increasing its ability to accept π electrons. Again, the relationship between steric and electronic effects is complex, but substituents that can hinder attack from either side of the plane of the dienophile generally have a detrimental effect on the rate of reaction. For example, the reactivity of a-substituted maleic anhydride derivatives was shown to be reduced when highly-branched substituents (e.g. isopropyl and cyclopentyl) were used. This was thought to be due to the low number of conformations that the substituent could adopt where attack from either side of the plane of the dienophile was possible. When less-highly-branched substituents were used, the number of conformations that the substituent could adopt was thought to be much greater. Certainly, the detrimental effect on the reactivity was either much less pronounced or non-existent [51].

### 2.3. Star Polymers

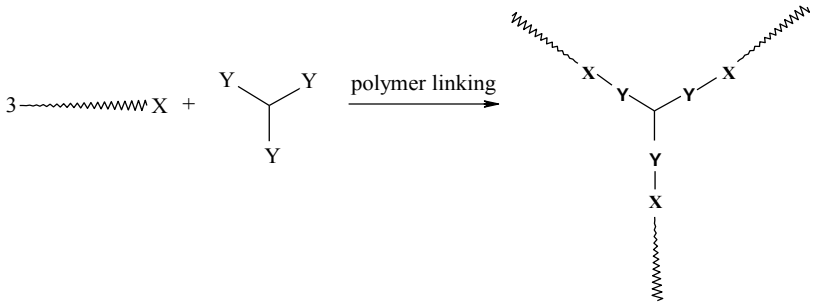
Polymers with narrow molecular and compositional (in the case of copolymers) dispersity and with well-defined architecture are essential for establishing

structure/properties relationships. These relationships are necessary to achieve one of the ultimate goals of polymer chemistry: designing molecules with predetermined properties. Star polymers, consisting of several identical linear chains linked together at one end of each chain (regular or symmetric stars), attracted the attention of scientists because they constitute the simplest form of branching.

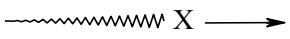
In principle, two basically different approaches are employed in the preparation of star polymers: one is by using coupling reactions or employing a linking agent (arm-first method), and the other is the core-first approach.

### 2.3.1. Star Polymers by the Arm-First Method

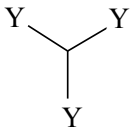
This technique involves the synthesis of preformed arms, usually through living polymerization followed by reaction with a multifunctional linking agent [52,53,1]. Schematic representation of star formation by the "arm-first method" is shown in scheme (2.12).




where;



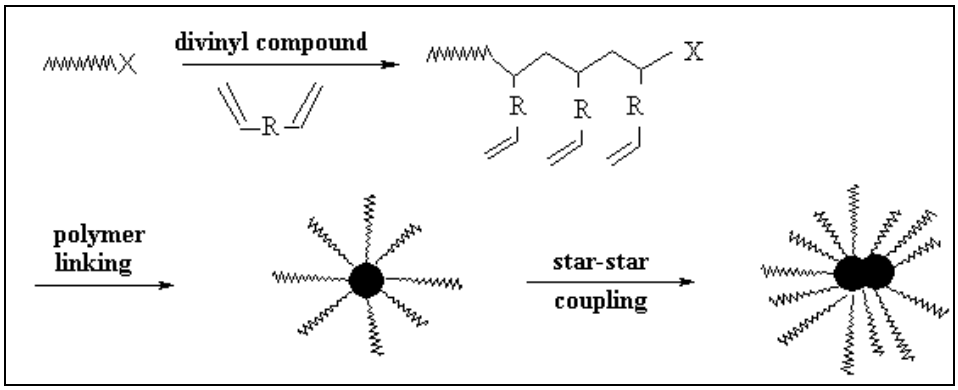

linear polymer chains




multifunctional linking agent

Scheme 2.12. Arm-first method

Star formation by using the arm first technique also involves the use of divinyl coupling reagents such as divinylbenzene (DVB) as a multifunctional linking agent. Initially, a few units of the divinyl coupling reagents are added to the macroinitiator chain ends to form short block copolymers.




Scheme 2.13. The proposed mechanism for the star polymer formation

The block copolymers containing the divinyl units then start to react with each other to form cross-linked cores, and this leads to the formation of star polymers. Finally star-star coupling can occur, leading to the formation of higher molecular weight stars. The proposed mechanism for the star polymer formation in the presence of a divinyl coupling reagent is presented in scheme (2.13) [54].

Coupling of monofunctional living chains with a difunctional reagent was first applied to living anionic polymerization. A similar approach has also been succesful with ATRP. There are several parameters in an ATRP that should be controlled carefully in order to maximize the yield of stars and prevent star-star coupling reactions.

### 2.3.2. Star Polymers by the Core-First Method

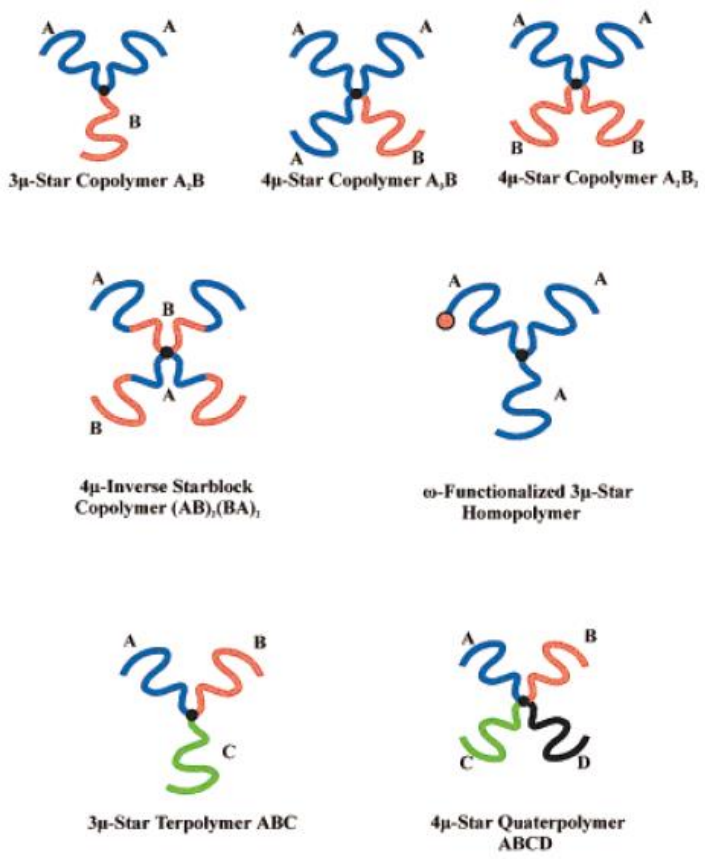
The core-first approach has come to maturity after it was shown in the1990s that stars of precise functionality could be obtained from multiionic initiators.

The core-first method involves the use of a multifunctional initiator, and the number of arms in the star polymer can be determined by the number of initiating sites on the initiator [55-57]. In this technique multifunctional initiators are used to grow chains from a central core resulting in macromolecules with well-defined structures in terms of both arm number and length. Furthermore the reaction consists solely of stars in the absence of linear polymers [58]. Most of the star polymers were prepared by this technique.

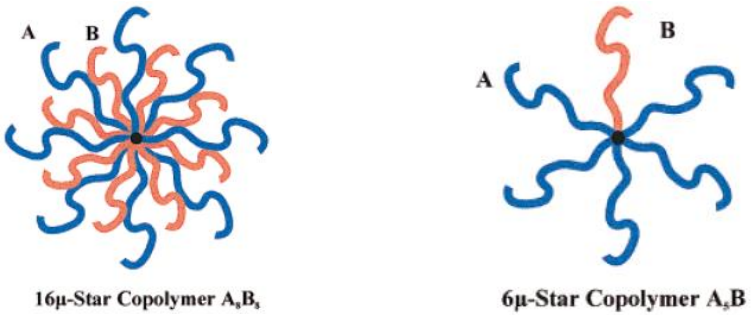
The first report of the core-first technique described the hexakis (bromomethyl) benzene-initiated ATRP of styrene, methyl acrylate, and methylmethacrylate [59], but its use was rather limited due to poor solubility in the reaction media.

### 2.3.3. Miktoarm ($\mu$) Star Polymers

Recently, the synthesis of megamolecules with unequal arms (molecular weight asymmetry) or with chemically different arms (chemical asymmetry) has been achieved (scheme 2.14a and 2.14b). The term miktoarm stars (coming from the greek word μικτός, meaning mixed) was adopted for the stars with chemical asymmetry. The term heteroarm stars (hetero coming from the greek word έτερος, meaning other) is not appropriate for this class of polymers, because it does not convey the concept of a group composed of dissimilar elements. Stars with molecular weight asymmetry can be considered miktoarm homopolymers. Stars having arms of similar chemical nature but different end groups also belong to this category. Finally, topologically asymmetric stars are also $\mu$-stars. They consist of diblock copolymer arms that are attached by different ends to the star center [1].




**Scheme 2.14a.** Miktoarm star ($\mu$-star) polymers




Scheme 2.14b. Miktoarm star ($\mu$-star) polymers.

The synthesis of asymmetric star-branched polymers is generally much more difficult than that of the corresponding regular stars. Two or more reactions with high (quantitative if possible) yield are required to introducing different arms, and isolation of the intermediate polymers may often be needed in each reaction step. Increasing attention has been paid to the synthesis of miktoarm star polymers in recent years due to their unique properties in solid state and in solution for selforganization. In a recent report, ABC miktoarm three-arm star polymers form novel multicompartment micelles in solution which is not possible from linear block copolymers so far. Therefore, synthesis of star block copolymers may have great potential to produce novel well-defined nanostructure by self-assembling [60].

Recently, the syntheses of a variety of asymmetric star-branched polymers by living radical polymerization systems have been reported by several research groups. Most stars have been synthesized by multi-functionalized initiators and therefore the issue of uniformity of the arm segments arises.

At the present time, most of well-defined asymmetric star-branched polymers are synthesized mainly by one of two methods using living anionic polymers. The first method is based on the successive reaction of living anionic polymers with multifunctional chlorosilanes, utilizing different reactivities of living polymers toward the Si–Cl bond. For example, the ABC asymmetric star-branched polymer was carefully synthesized by the following three reaction steps: (1) polyisoprenyllithium was reacted with a large excess (a 60-fold excess) of methyltrichlorosilane, followed by removal of the excess methyltrichlorosilane; (2) a stoichiometric amount of PSLi was slowly added to the resulting polyisoprene having terminal $SiCl_2$ functionality; and (3) the in-chainfunctionalized polyisoprene-block-polystyrene with SiCl function thus prepared was in situ reacted with a small

excess of poly(1,3-butadienyl)lithium. The object ABC star-branched polymer was obtained after fractionation to remove unreacted polymers.

Similarly, various asymmetric stars such as $AB_2$, $AB_3$, $A_2B_2$, $A_8B_8$, and ABCD types have been synthesized by this method, although the acceptable living polymers are limited to those of styrene and 1,3-diene monomers. The second method is based on the chemistry of functionalized DPE derivatives. Fujimoto and coworkers first demonstrated the utility of DPE derivative for the synthesis of asymmetric starbranched polymers. An ABC asymmetric star was synthesized by the living linking reaction of a non-polymerizable DPE-functionalized poly(dimethylsiloxane) macromonomer with PSLi, followed by initiation of anionic polymerization of tert-butyl methacrylate. Almost at the same time, Quirk and his coworkers reported the successful synthesis of a series of $A_2B_2$ stars by the living linking reaction of two equivalents of PSLi with 1,3-bis(1-phenylethenyl)- benzene, comprising two DPE moieties, followed by initiating the polymerization of 1,3-butadiene with the two anions generated. The synthetic utility of DPE derivatives lies in the specific reactivity of DPE capable of participating two reactions (living linking and polymerization reactions) to link different two arms. Subsequently, various asymmetric starbranched polymers by the similar methods have been synthesized by several research groups. Although progress has thus been made in the synthesis of asymmetric star-branched polymers, structural and architectural variations of well-defined asymmetric star-branched polymers are still limited from a synthetic points of view. Therefore, a new development of general and versatile synthetic methods is desired even at the present time [61].

# 3. EXPERIMENTAL PART

## 3.1. Materials

Styrene (St, 99%, Merck) and *tert*-butylacrylate (*t*BA, 99%, Aldrich) were passed through basic alumina column to remove inhibitor and then distilled over $CaH_2$ *in vacuo* prior to use. *N, N, N', N'', N''*-pentamethyldiethylenetriamine (PMDETA, Aldrich) was distilled over NaOH prior to use. Poly(ethylene glycol) (PEG, Acros) ($M_n$=550) was dried over anhydrous toluene by azeotropic distillation. 4-dimethylaminopyridinium 4-toluenesulphonate (DPTS) was obtained according to from a published procedure [62]. Tetrahydrofuran (THF, 99.8%, J.T. Baker) was dried and distilled over $LiAlH_4$. Dichloromethane was purchased from Aldrich and used after distillation over $P_2O_5$. 2,2-bis(hydroxymethyl)propanoic acid (bis-MPA, 99% Across), triethylamine ($Et_3N$, 99% Merck), 2-Bromoisobutryl bromide (99% Aldrich), 4-dimethylaminopyridine (DMAP, 99% Aldrich), *N*,*N*-dicyclohexylcarbodiimide (DCC, 99% Across), 2,2,6,6-tetramethylpiperidinyl-1-oxy (TEMPO, 98% Across), 2,2-dimethoxypropane (98% Across), Benzoyl peroxide (BPO, 77% Fluka), absolute ethanol (99.5% J.T.Baker) were used as received. All other reagents were purchased from Aldrich and used as received.

## 3.2. Syntheses

### 3.2.1. Synthesis of Initiator

#### 3.2.1.1. Synthesis of benzoic acid 2-phenyl-2-(2,2,6,6-tetramethyl-piperin-1-yloxy)-ethyl ester [1]

In a 500 mL of two-necked round bottom flask, equipped with a magnetic stirrer, TEMPO (2,2,6,6-tetramethylpiperidinyl-1-oxy) (3 g, 19.2 mmol) and BPO (4.7 g, 19.2 mmol) were dissolved in 300 mL of freshly distilled Styrene, then flask conducted three times evacuation and subsequent argon purging. The solution was kept for 30 minutes stirring at 90 $^oC$ in an oil bath. After that period more styrene

removed via back distillation and flask dissolved in 100 mL of ethyl acetate then extracted two portions (50 mL) of NaOH (1%). The combined organic phase was dried with $Na_2SO_4$ and solvent evaporated. The crude product purified by column chromatography over silica gel eluting just with dichloromethane, and the product fully purified by recrystallization from cold hexane concentrated to yield 2.4 g (6.3 mmol, 67%) as white needles.

#### 3.2.1.2. Synthesis of 2-phenyl-2-(2,2,6,6-tetramethyl-piperin-1-yloxy)-ethanol [2]

Product **1** (2.4g, 6.3 mmol) was dissolved in 35 mL of absolute ethanol and 8.5 mL of 2 N KOH and kept for 5 h to reflux. After the product is extracted with water and dichloromethane (1:1). The combined liquid phase is again extracted with dichloromethane and combined organic phase dried with $Na_2SO_4$, evaporation of the solvent yielded 1.66g (5.99 mmol, 96%) as yellow viscous liquid without further purification.

#### 3.2.1.3. Synthesis of 2,2,5-trimethyl-[1,3]dioxane-5-carboxylic acid [3]

The 2,2-bis(hydroxymethyl)propanoic acid (4 g, 29.84 mmol) along with *p*-TSA (0.112, 0.58 mmol), and 2,2-dimethoxypropane (5.6 mL, 44.8 mmol) dissolved in 20 mL of dry acetone , and stirred 2 h at room temperature. In the vicinity of 2 h, while stirring continued the reaction mixture was neutralized with 3 mL of totally $NH_4OH$ (25%), and absolute ethanol (1:1), filtered off by-products and subsequent dilution with dichloromethane (50 mL) , and once extracted with distilled water (20 mL). The organic phase dried with $Na_2SO_4$, concantrated to yield 3.7 g (21.2 mmol, 71%) as white solid after evaporation of the solvent.

#### 3.2.1.4. Synthesis of 2,2,5-trimethyl-[1,3]dioxane-5-carboxylic acid 2-phenyl-2-(2,2,6-trimethyl-piperidin-1-yloxy)-ethyl ester [4]

Compound **2** (1.66 g, 5.99 mmol) was dissolved in 10 mL of dry dichloromethane along with compound **3** (1.095 g, 6.29 mmol), and DPTS (0.280 g, 0.89 mmol) were added in that order, after stirring 5 minutes at room temperature DCC (1.59 g, 7.740 mmol) dissolved in 5 mL $CH_2Cl_2$ was added. Reaction mixture was then left overnight at room temperature to stir. After filtration off the urea byproduct, the solvent removed, and the remaining product was purified by column chromatography over silica gel eluting with hexane/ethylacetate (9:1). To remove any other byproduct

after column 10 mL of cold hexane was added, and filtrate off, solvent removed in vacuum to give the yield 1.733 g (4 mmol, 66%) as pale yellow

### 3.2.1.5. Synthesis of 3-hydroxy-2-hydroxymethyl-2-methyl-propionic acid 2-phenyl-2-(2,2,6,6-tetramethyl-piperidin-1-yloxy)-ethyl ester [5]

Compound **4** (1.733 g, 4 mmol) was dissolved in 12 mL of THF and 12 mL of 1 M HCl. The reaction mixture was then stirred for 2 h at room temperature. The precipitated product was filtered off, after removing of THF in vacuum, the reaction mixture extracted with 40 mL of $CH_2Cl_2$, and same amount of distilled water. The combined organic phase dried with $Na_2SO_4$, evaporation of the solvent concentrated to yield 1.214 g (3.089 mmol, 77%) as white solid.

### 3.2.1.6. Synthesis of 2-(2-bromo-2-methyl-propionyloxymethyl)-3-hydroxy-2-methyl propionic acid 2-phenyl-2-(2,2,6,6-tetramethyl-piperidin-1-yloxy)-ethyl ester [6]

Compound **5 (**1.554 g, 3.95 mmol) was dissolved in 20 mL of $CH_2Cl_2$, and $Et_3N$ (1.21 mL, 8.7 mmol) was added. The reaction mixture was cooled to 0 $^oC$. 2-Bromoisobutryl bromide was added dropwise within 30 minutes. The reaction mixture was stirred 4 h at room tempeature. After filtration off little byproduct, the mixture extracted with $CH_2Cl_2$, and saturated aq. $NaHCO_3$. The water phase again extracted with $CH_2Cl_2$, and combined organic phase dried with $Na_2SO_4$. The solution was concantrated, and the crude product was purified by column chromatography over silica gel eluting with hexane/ethylacetate (10:1) to give the yield 1.79 g (3.31 mmol, %83) as pale yellow.

### 3.2.1.7. Synthesis of succinic acid mono-anthracen-9-ylmethyl-ester [7]

9-Anthryl methanol (4.16 g, 20 mmol) was dissolved in 150 mL of $CH_2Cl_2$. To the reaction mixture were added $Et_3N$ (14 ml, 100 mmol) and DMAP (2.44 g, 20 mmol). The succinic anhydride (8 g, 80 mmol) was added and stirred overnight at room temperature. The reaction solution was poured into ice-cold water (150 ml) and extracted with $CH_2Cl_2$. The organic phase again extracted with 1M HCl (150 ml).Water phases extracted with $CH_2Cl_2$. Combined organic phase dried over $Na_2SO_4$ and concentrated to yield 5.85 g (117 mmol, %95) as green solid. $^1H$ NMR

($CDCl_3$, O) 7.43-8.50 (m, 9 Ar*H* of anthracene) 6.16 (s, 2H, C$H_2$-O), 2.66 (t, 4H, -O-C$H_2$-C$H_2$-O-)

### 3.2.1.8.Synthesis of succinic acid anthracen-9-ylmethyl ester 3-(2-bromo-2-methyl-propionyloxy)-2-methyl-2-[2-phenyl-2-(2,2,6,6-tetramethyl-piperidin-1-yloxy)-ethoxy- carbonyl]-propyl ester [8]

Miktofunctional initiator, **(6)**, (0.620 g, 1.14 mmol) was dissolved in 10 mL of dry $CH_2Cl_2$. To the reaction mixture was added **7** (0.384 g, 1.25 mmol), and DPTS (0.071 g, 0.23 mmol) in that order. After stirring 5 minutes at room temperature, dicyclohexylcarbodiimide (DCC) (0.257 g, 1.24 mmol) dissolved in 5 mL of $CH_2Cl_2$ was added and stirred overnight at room temperature. After filtration off the urea byproduct, the solvent was removed, and the remaining product was purified by column chromatography over silica gel eluting with hexane/ethylacetate (10:1) and then with (4:1) to give **8** as pale yellow oil (Yield: 0.6 g, 63%).

### 3.2.2. Synthesis of 4-maleimido-benzoic Acid [9]

In a three necked flask provided with a reflux condenser, 4-amino benzoic acid (13.7 g, 100 mmol) was dissolved in DMF (150 ml). Under mechanical stirring, a solution of maleic anhydride (21.56 g, 220 mmol) in DMF (80 ml) was added dropwise through a dropping funnel under $N_2$ atmosphere during 30 min. After the addition, the thick suspension was stirred at room temperature for 1 h. Afterward acetic anhydride (100 ml, 336 mmol), sodium acetate (2.5 g, 30 mmol) were added. The reaction mixture was heated at 45 $^oC$ for 2 h. then overnight at room temperature under stirring. After cooling to room temperature, the reaction mixture was poured into ice-cold water (100 ml). The product was filtered off and dried in a vacuum oven. The crude product was recrystallized from water -ethanol (1:4) to give the pure product 11 g ( %51 )yield) as white solid.

### 3.2.3. Synthesis of 4-maleimido-benzoylchloride [10]

4-maleimido-benzoic acid (9) (5 g, 23.2 mmol) was dissolved in excess thionyl chloride under nitrogen atmosphere. After the mixture was refluxed for overnight, excess thionyl chloride was removed under reduced pressure and the product was crystallized from benzene to give **10** as yellow solid (Yield: 4.23 g, 78%).

### 3.2.4. Esterification of PEG with 4-maleimido-benzoylchloride [11]

PEG ($M_n$= 550) (2 g, 3.63 mmol) was dissolved in 10 mL of THF, and $Et_3N$ (0.8 mL, 5.44 mmol) was added. The reaction mixture was cooled to 0 $^oC$ and a solution of 4-maleimidobenzoylchloride **(10)** (1.7 g, 7.26 mmol) in 10 mL of THF was added drop wise within 30 minutes. The reaction mixture was stirred overnight at room temperature. After filtration off the salt, the solution was concentrated and the viscous brown color product was purified by column chromatography over silica gel eluting with $CH_2Cl_2$/ethylacetate (1:1) and then with $CH_2Cl_2$/MeOH (10:1) to give **11** as viscous yellow oil (Yield: 1.76 g, 65%). $M_{n,theo}$ = 750; $M_{n,NMR}$ = 732; $M_{n,GPC}$ = 740; $M_w/M_n$ = 1.07. $^1$H NMR ($CDCl_3$, O) 8.14 (d, 2H, OC=OAr*H*), 7.49 (d, 2H, Ar*H*NC=O), 6.88 (s, 2H, NC=OC*H*=C*H*), 4.48 (t, 2H, PEG-OC$H_2$C$H_2$OC=O), 3.82 (t, 2H, PEG-OC$H_2$C$H_2$OC=O), 3.67-3.62 (m, 4H, -OC$H_2$C$H_2$- of PEG), 3.54 (t, 2H, $CH_3$-O-C$H_2$C$H_2$-O), 3.37 (s, 3H, C$H_3$-OC$H_2$C$H_2$).

### 3.2.5. Synthesis of 9-anthyrylmethyl 2-bromo-2-methyl propanoate [12]

To a round bottom flask were added 9-anthracene methanol (1.5 g, 7.18 mmol), triethylamine (1.2 mL, 8.6 mmol), DMAP (0.175 g, 1.436 mmol), and 20 ml of dry THF. To the reaction mixture, stirred at 0 $^oC$ under nitrogen was added drop-wise 2-bromo isobutyrl bromide (1.82 g, 7.89 mmol) in 10 ml of dry THF over a period of 30 min. The reaction mixture was stirred at room temperature overnight. The salt was removed by filtration and after THF evaporation, crude product was extracted with $CH_2Cl_2$ and dilute $NaHCO_3$ aqueous solution for two times The water phase again extracted with $CH_2Cl_2$, and combined organic phase dried with $Na_2SO_4$ over anhydrous sodium sulfate ($Na_2SO_4$). $CH_2Cl_2$ was removed and the crude product was purified by column chromatography over silica gel eluting with hexane/ethylacetate (9:1) to give **12** as solid yellow 1,78 g (4,97 mmol, %70) as yellow solid. (Yield: 1.78 g, 70 %). $^1$H NMR ($CDCl_3$, O). 7.43-8.52 (m, 9 Ar*H* of anthracene) 6.21 (s, 2H, C$H_2$-O), 1.87 (s, (C$H_3$)$_2$-C-Br).

### 3.3. Model Diels-Alder Reactions

#### 3.3.1. DA reaction between *N*-ethyl maleimide and 9-anthyrylmethyl 2-bromo-2-methyl propanoate (12): [13]

A model DA reaction was carried out in THF at reflux temperature. In a 50 mL of round bottom flask, *N*-ethyl maleimide (0.18 g, 1.44 mmol) and **12** (0.51 g, 1.44 mmol) were dissolved in 15 mL of THF and refluxed overnight under nitrogen. The solution was then concentrated to dryness and purified by column chromatography over silica gel eluting with hexane/ethylacetate (10:1) and then with (1:1) to give 0.66 g (96%) as a pale yellow solid, $^1$H NMR ($CDCl_3$, O) 7.36-7.28 (m, 4H, Ar*H*), 7.16-7.14 (m, 4H, Ar*H*), 5.60, 5.48(dd, 2H, C*H*$_2$OC=O), 4.76 (bs, 1H, C*H*), 3.23 (bs, 2H, C*H*$_2$N), 3.11-3.08 (m, 2H, NC=OC*H*), 1.95 (d, 6H, CBr(C*H*$_3$)$_2$), 0.36 (t, 3H, NCH$_2$C*H*$_3$).

#### 3.3.2. DA reaction between PEG-maleimide (11) and 9-anthyrylmethyl 2-bromo-2-methyl propanoate (12): [14]

Into a 50 mL round bottom flask, PEG-maleimide, **(11)**, (0.378 g, 0.5 mmol), **12** (0.18 g, 0.5 mmol) and 20 mL of THF were added. The reaction mixture was refluxed overnight under nitrogen. Solvent was removed and the product was purified by column chromatography (silica gel) eluting once with $CH_2Cl_2$/ethylacetate (1:1) to remove the unreacted anthracene derivative and then with $CH_2Cl_2$/MeOH (10:1) to give 14. Yield: 0.53 g (95%). $^1$H NMR ($CDCl_3$, O) 7.96 (d, 2H, OC=OAr*H*), 7.46-7.37 (m, 4H, Ar*H*), 7.25-7.22 (m, 4H, Ar*H*), 6.64 (d, 2H, Ar*H*NC=O), 5.64 and 5.49 (dd, 2H, C*H*$_2$OC=O), 4.88 (s, 1H, C*H*, bridge-head proton), 4.42 (t, 2H, PEG-OCH$_2$C*H*$_2$OC=O), 3.77 (t, 2H, PEG-OC*H*$_2$CH$_2$OC=O), 3.63 (m, 4H, -OC*H*$_2$C*H*$_2$- of PEG), 3.54-3.50 (m, 4H, NC=OC*H*-*CH* and $CH_3$-O-C*H*$_2$CH$_2$-), 3.36 (s, 3H, C*H*$_3$-OCH$_2$CH$_2$), 1.98 (d, 6H, CBr(C*H*$_3$)$_2$).

### 3.4. Preparation of PEG-PSt-P*t*BA Miktoarm Star Terpolymer

#### 3.4.1. DA reaction of PEG-maleimide (11) with the initiator (8): [15]

A solution of **8** (0.322 g, 0.387 mmol) in 10 mL of THF was added to 0.289 g of PEG-maleimide, **(11)**, (0.387 mmol) in 10 mL of THF. The mixture was purged with nitrogen for 1h and refluxed for 48 h at 75 $^o$C. The solvent was removed and the

remaining product was purified by column chromatography over silica gel eluting with $CH_2Cl_2$/ethylacetate (1:1) and then with $CH_2Cl_2$/methanol (10:1) to give **15** as viscous pale yellow liquid (Yield: 0.58 g, 95 %). $M_{n,theo}$ = 1580; $M_{n,NMR}$ = 1600; $M_{n,GPC}$ = 1600; $M_w/M_n$ = 1.01.

### 3.4.2. Preparation of PEG-PSt precursor (16) using PEG-macroinitiator (15) by SFRP of St: [16]

PEG-PSt precursor, **(16)**, was prepared using SFRP of St (1.5 mL, 13.1 mmol) in the presence of macroinitiator, **(15)**, (0.210 g, 0.13 mmol). The reaction mixture was degassed by three freeze-pump-thaw cycles and left in vacuum. The tube was then placed in an oil bath thermostated at 125 $^oC$ for 15 h. The polymerization mixture was diluted with THF, and precipitated in methanol. The PEG-PSt precursor, **(16)**, was dried for 24 h in a vacuum oven at 50 $^oC$. Conv. 85%; $M_{n,theo}$ = 10450; $M_{n,NMR}$ = 10900; $M_{n,GPC}$ = 10100; $M_w/M_n$ = 1.09.

### 3.4.3. Preparation of PEG-PSt-P*t*BA miktoarm star terpolymer (17) by ATRP of *t*BA: [17]

Miktoarm star terpolymer, PEG-PSt-P*t*BA, was prepared by ATRP of *t*BA using **16** as a macroinitiator. Into a 25 mL of Schlenk tube, *t*BA (2 mL, 13.6 mmol), PMDETA (0.006 mL, 2.87 X $10^{-5}$ mol), CuBr (0.004 g, 2.78 X $10^{-5}$ mol) and PEG-PSt precursor **(16)** (0.296 g, 2.72 X $10^{-5}$ mol) were added in that order and the reaction mixture was degassed by three freeze pump- thaw cycles and left in vacuum. The tube was then placed in an oil bath thermostated at 80 $^oC$ for 240 min. After that the dark green polymerization mixture was diluted with THF, and passed through a basic alumina column to remove the catalyst, and precipitated in water : methanol (1: 4). The polymer, **(17)**, was dried for 24 h in a vacuum oven at 50 $^oC$. Conv. 4%; $M_{n,theo}$ = 13500; $M_{n,NMR}$ = 14000; $M_{n,GPC}$ = 12600; $M_w/M_n$ = 1.14.

### 3.5. Characterization

The $^1H$ and $^{13}C$ NMR spectra were recorded on a Bruker NMR Spectrometer (250 MHz for proton and 62.89 MHz for carbon) in $CDCl_3$. Gel permeation chromatography measurements were obtained from an Agilent instrument (Model 1100) consisting of a pump, refractive index and UV detectors, and four Waters

Styragel columns (HR 5E, HR 4E, HR 3, and HR 2). THF was used as eluent at a flow rate of 0.3 mL/min at 30 $^{o}$C. Toluene was as an internal standard. Data analyses were performed with PL Caliber Software. The molecular weight of the polymers was calculated on the basis of linear polystyrene standards (Polymer Laboratories) and the conversions were determined by gravimetrically. UV spectra were recorded on a Perkin Elmer Lambda 2 spectrophotometer in $CH_2Cl_2$. Differential Scanning Calorimetry (DSC) was measured on a DSC Q100 (TA Instruments) at a heating rate of 10 $^{o}$C/min under nitrogen atmosphere. All data were collected from a second heating cycle and the glass transition temperatures ($T_g$) were calculated as a midpoint of thermograms.

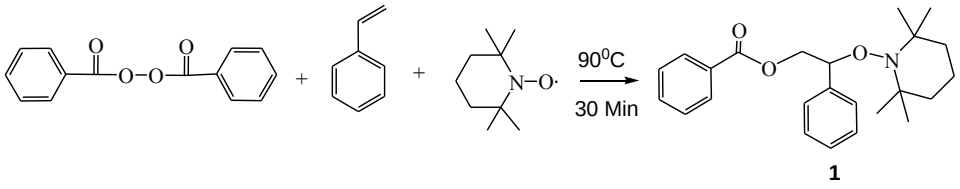
## 4. RESULTS and DISCUSSION

Generally two methods have been applied to achieve miktoarm star polymers: "core in" and "core out". We here combined these two methods to obtain PEG-PSt-P*t*BA miktoarm star terpolymer. First PEG-maleimide, **(11)**, was reacted with **8** by DA reaction (core in). Second a previously obtained macroinitiator, **(15)**, is consequently used in SFRP of St and ATRP of *t*BA (core out). Since the DA reaction is a key step for the preparation of miktoarm star polymer, a model DA reaction between *N*-ethyl maleimide and **12** is investigated. Moreover, on the basis of polymer analogous DA reactions, the feasibility of the reaction between PEG-maleimide **(11)** and **12** is also demonstrated.

### 4.1. Syntheses

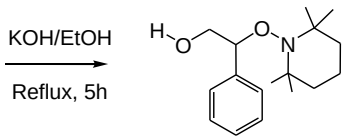
#### 4.1.1. Synthesis of Initiator

The initiator synthesis was carried out as follows: First of all, the synthesis of benzoic acid 2-phenyl-2-(2,2,6,6-tetramethyl-piperidin-1-yloxy)-ethyl ester **(1)** was carried out by heating styrene in the presence of benzoyl peroxide and TEMPO for 30 minutes. The hydrolysis of ester was then carried out to give the 2-phenyl-2-(2, 2, 6, 6-tetramethyl-piperidin-1-yloxy)-ethanol **(2)**. The characteristic peak of aromatic protons adjacent to ester group at δ 7.9 ppm completely disappeared after hydrolysis. Moreover, the new signals appeared at δ 5.9 ppm of –OH and the shifts of the $–CH_2$ and –CH protons adjacent to hydroxyl and aromatic group, respectively, clearly confirm the successful hydrolysis. The $^1$H NMR spectra of the corresponding ester and alcohol precursors are presented in Figures 4.1 and 4.2, respectively.




1

(4.1)




2

(4.2)

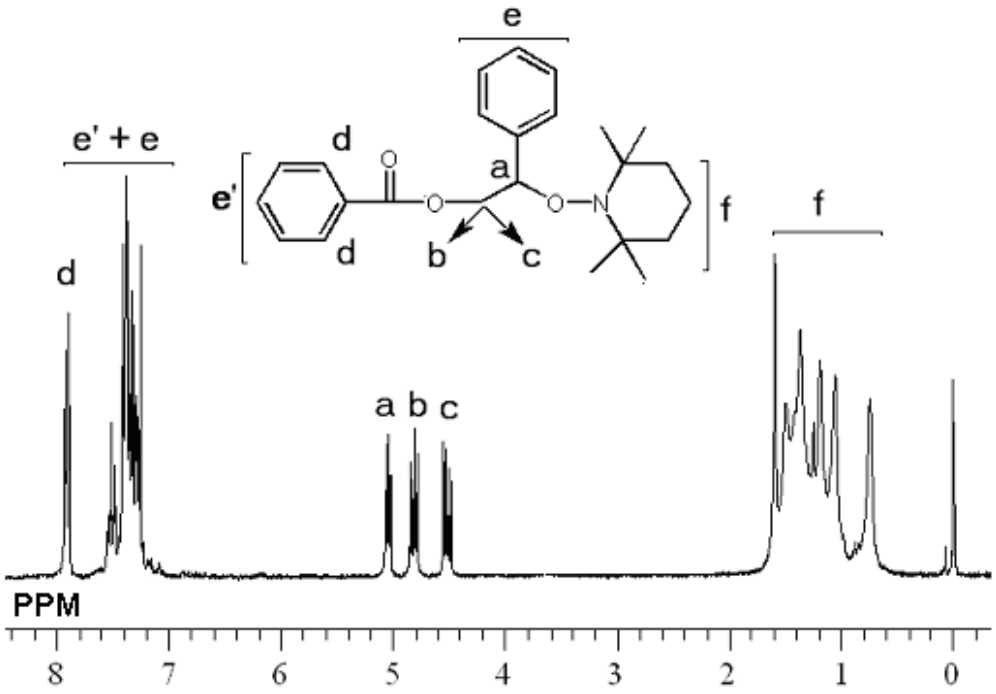



**Figure 4.1 :** The $^{1}H$ NMR spectrum of benzoic acid 2-phenyl-2-(2, 2, 6, 6-tetramethyl-piperin-1-yloxy)-ethyl in $CDCl_3$.

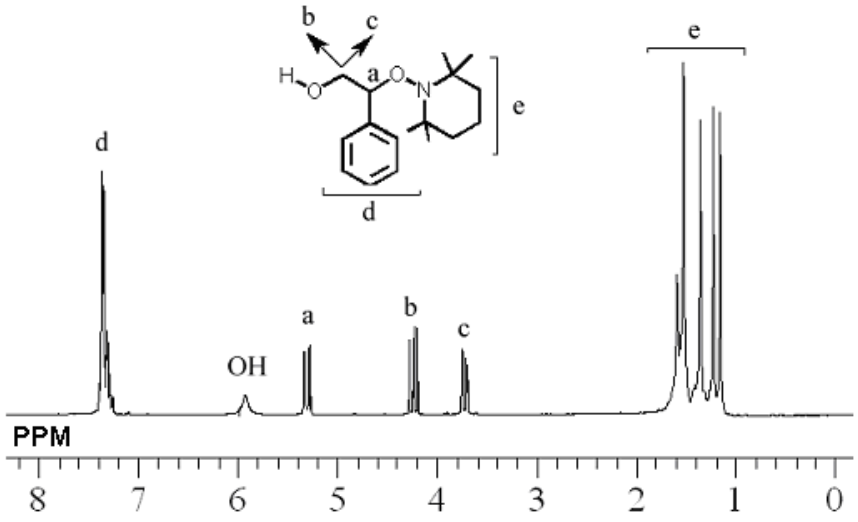
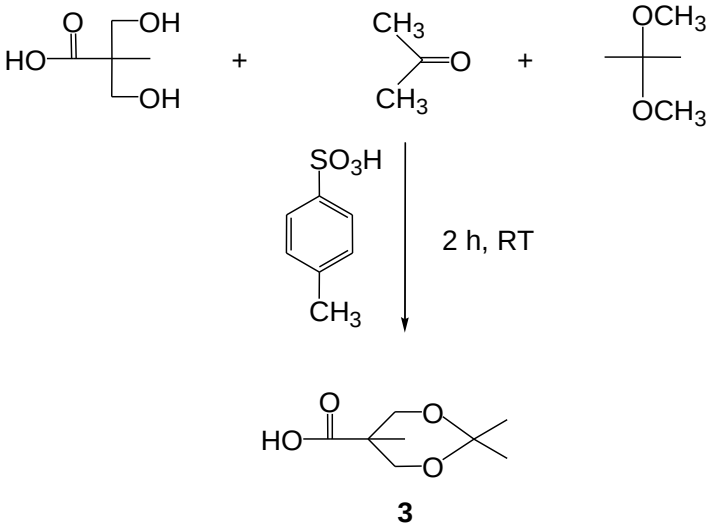



**Figure 4.2 :** The $^{1}H$ NMR spectrum of 2-phenyl-2-(2, 2, 6, 6-tetramethyl-piperin-1-yloxy)-ethanol in $CDCl_3$.

In order to convert the hydroxyl functionality at compound **2** into two hydroxyl functionalities, successive protection, esterification and deprotection reactions were realized. For this purpose, the hydroxyl protected acidic compound, **(3)**, was synthesized according to the following reaction.

In this reaction, 2, 2-bis (hydroxymethyl)-propanoic acid was reacted with excess amount of dry acetone using *p*-toluene sulfonic acid as catalyst. Additionally, 2,2-dimethoxy-propane was deliberately used to provide acetone during the reaction. The $^{1}H$ NMR spectrum of the compound, **(3)**, is shown in Figure 4.3.




(4.3)

**3**

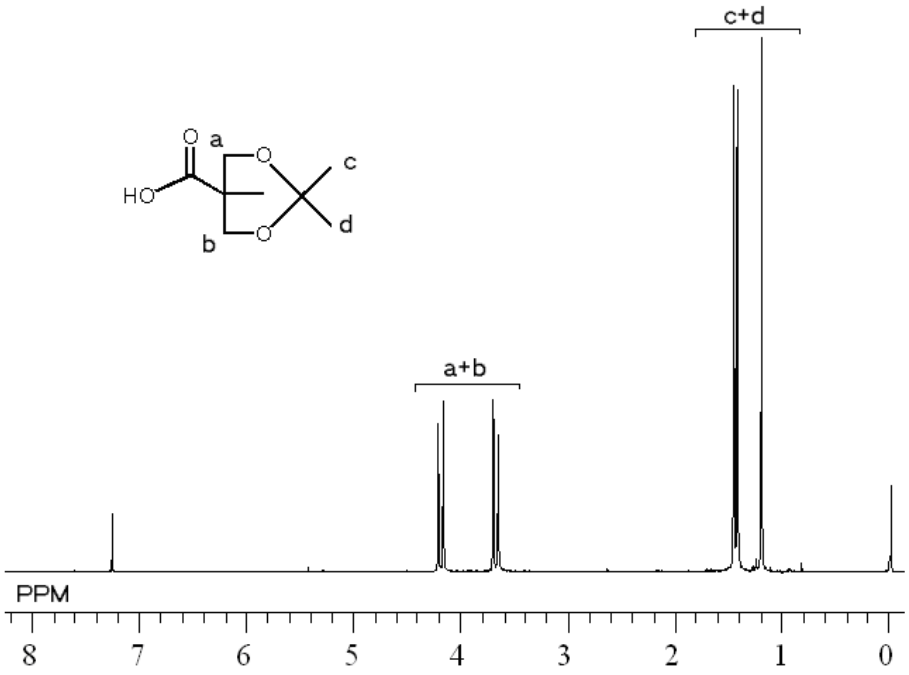
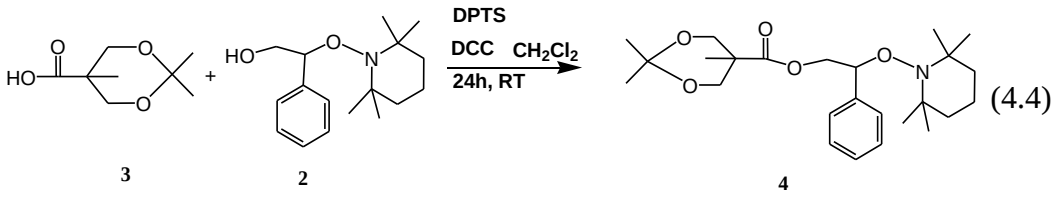
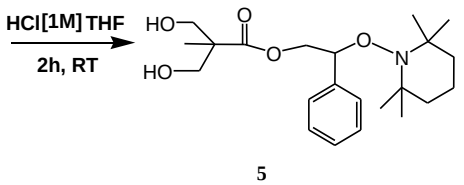



**Figure 4.3 :** The $^{1}H$ NMR spectrum of 2,2,5-trimethyl-[1,3]dioxane-5-carboxylic acid in $CDCl_3$.

Subsequent esterification reaction between alcohol and hydroxyl protected acid was carried out using catalytic amount of DPTS (dimethylamino-4-toluene-sulfonate). Although this procedure was reported to be a suitable method for the esterification reaction [63], the main drawback of this system is related to the difficulties arising from the removal of formed urea by product. However, this was overcomed by further precipitation followed by filtration method. The $^{1}H$ NMR spectrum of the compound, **(4),** is shown in Figure 4.4.




**3** **2** **4** (4.4)




**5** (4.5)

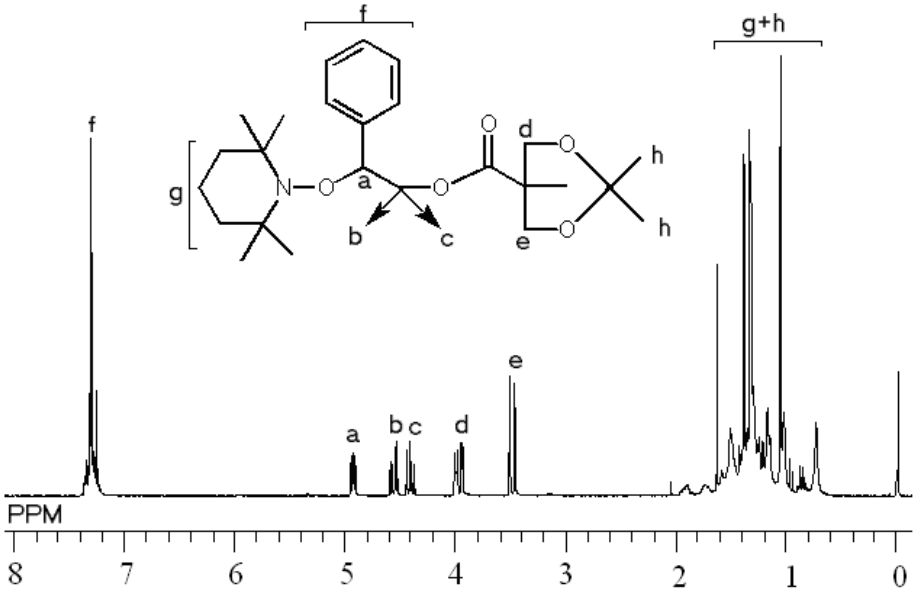



**Figure 4.4 :** The $^{1}$H NMR spectrum of 2,2,5-trimethyl-[1,3]dioxane-5-carboxylic acid 2-phenyl-2-(2,2,6-trimethyl-piperidin-1-yloxy)-ethyl ester in $CDCl_3$.

Finally, deprotection step was easily achieved by acidic hydrolysis using 1 M HCl and THF at room temperature. $^{1}$H NMR spectrum of the desired compound, **(5)**, is shown in Figure 4.5. From the NMR spectrum -OH protons (e-e') at δ 2.7 ppm suggests that deprotection step was carried out successfully

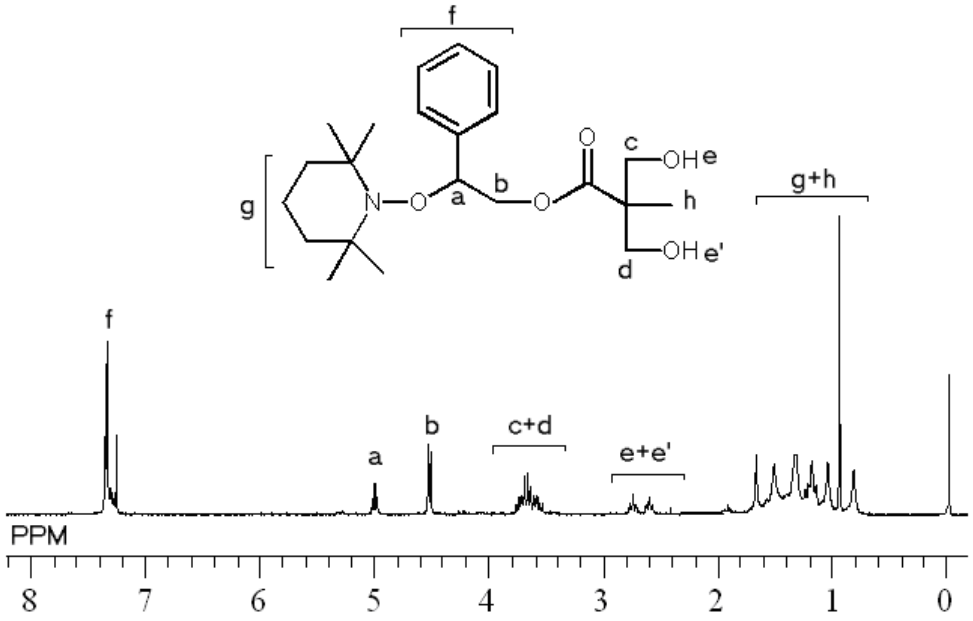
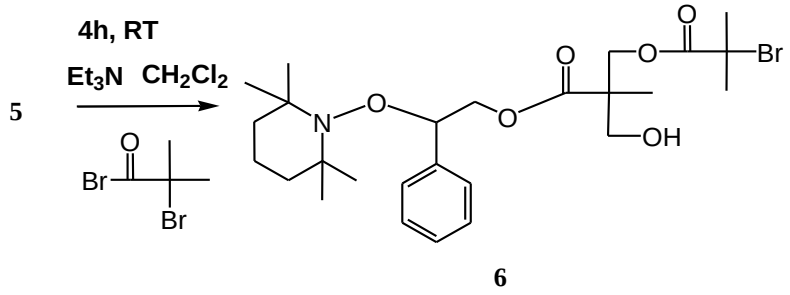



**Figure 4.5 :** The $^{1}$H NMR spectrum of 3-hydroxy-2-hydroxymethyl-2-methyl-propionic acid 2-phenyl-2-(2,2,6,6-tetramethyl-piperidin-1-yloxy)-ethyl ester in $CDCl_3$.

In order to introduce ATRP functionality into the synthesis, second esterification reaction was achieved. In this connection, it should be pointed out that at this step

severe reaction conditions may cause the hydrolysis of the ester groups present in the structure. Therefore, the esterification process was performed at $^{o}$C and 2-bromoisobutryl bromide was added in a dropwise manner. The $^{1}$H NMR spectrum of the compound **6** showed that the –OH protons of compound **5** at δ 2.7 ppm completely removed. Moreover, the new –OH proton at δ 2.2 ppm belongs to $–CH_2$ group, the shift of the $-CH_2$ protons adjacent to ATRP functionality to δ 4.1 ppm and the $–CH_3$ protons on ATRP functionality at δ 1.89 ppm indicate that esterification reaction was carried out successfully. The $^{1}$H NMR spectrum of the resulting compound, **(6),** is shown in Figure 4.6.




(4.6)

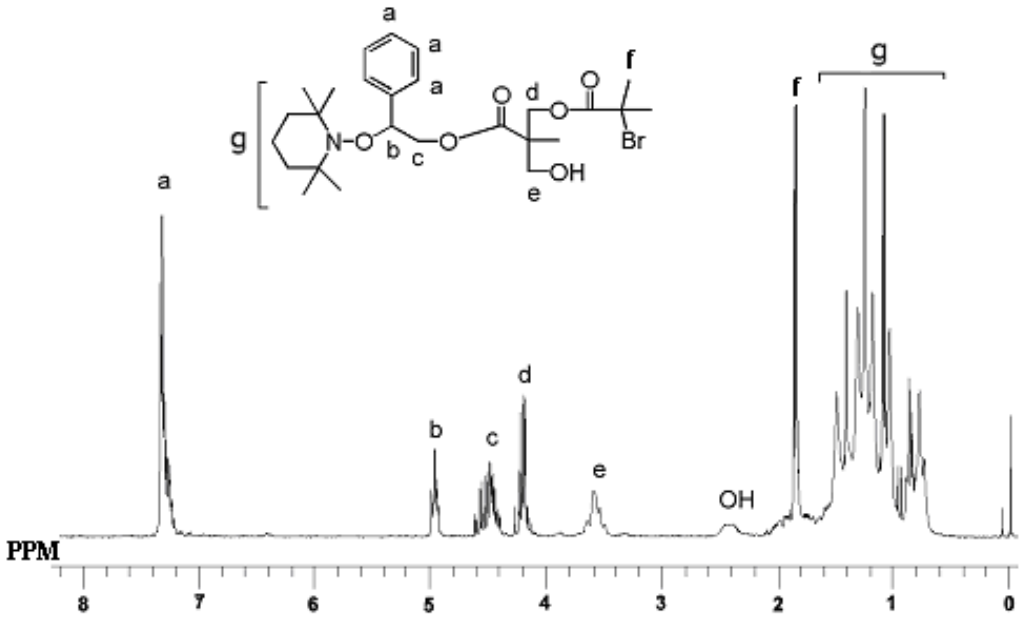
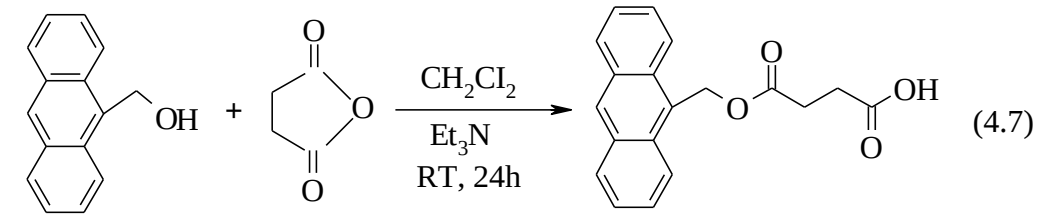



**Figure 4.6 :** The $^{1}$H NMR spectrum of 2-(2-bromo-2-methyl-propionyloxymethyl)-3-hydroxy-2-methyl propionic acid 2-phenyl-2-(2,2,6,6-tetramethyl-piperidin-1-yloxy)-ethyl ester in $CDCl_3$.

Succinic acid mono-athracen-9-ylmethyl ester, **(7),** was synthesized upon the reaction with 9-anthrylmethanol and succinic anhydride [64]. The $^{1}$H NMR spectrum of the compound, **(7)**, is shown in Figure 4.7.

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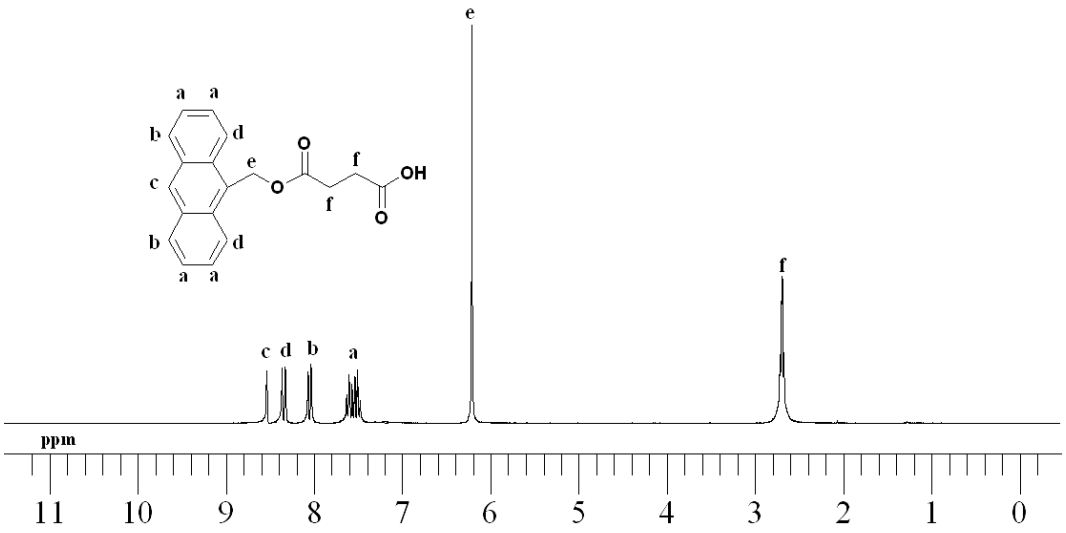
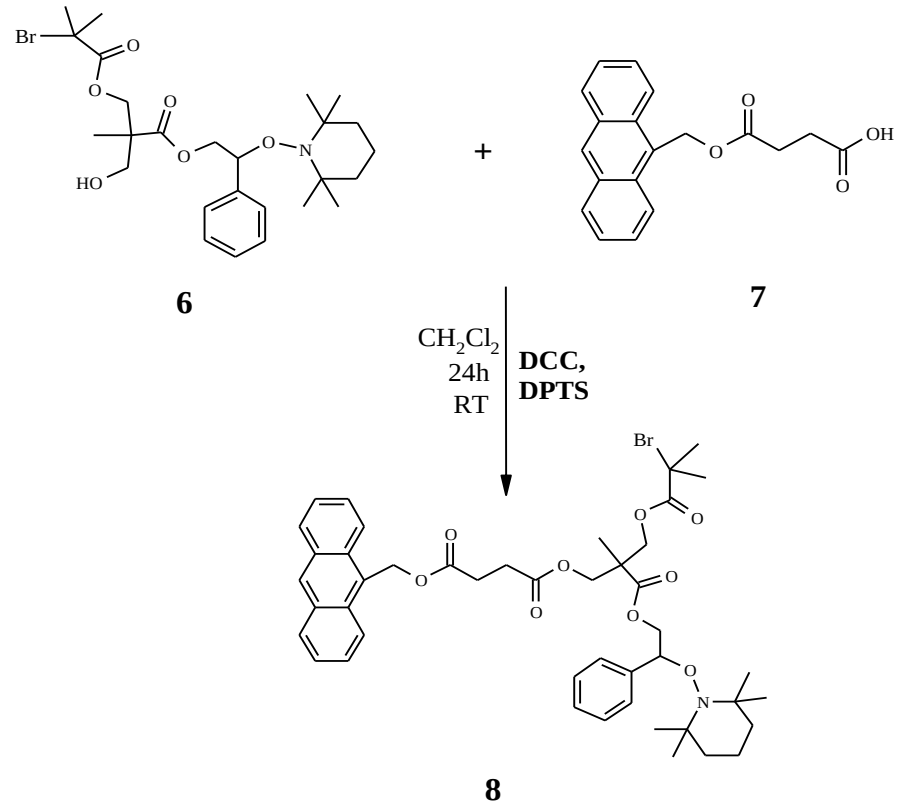



**Figure 4.7 :** The $^1$H NMR spectrum of succinic acid mono-anthracen-9-ylmethyl-ester in $CDCl_3$.

The synthesis of miktofunctional initiator, (**8)**, containing anthracene, TEMPO and *tert*bromide functional groups was carried out by reacting **6** with **7** (Scheme 4.8). $^1$H NMR spectrum of **8** indicated a successful esterification (Figure 4.8).

A broad peak of -$CH_2O$*H* at 3.55 ppm was disappeared and a corresponding ester (C*H*$_2$OC=O) signal was emerged at 4.09 ppm. Furthermore, from the spectrum, aromatic hydrogens of anthracene, C*H*$_2$-C*H* protons adjacent to TEMPO, and C*H*$_3$ protons of *tert*– bromide functionality could easily be detected at 8.5-7.48, 4.93-4.36, and 1.81 ppm, respectively.



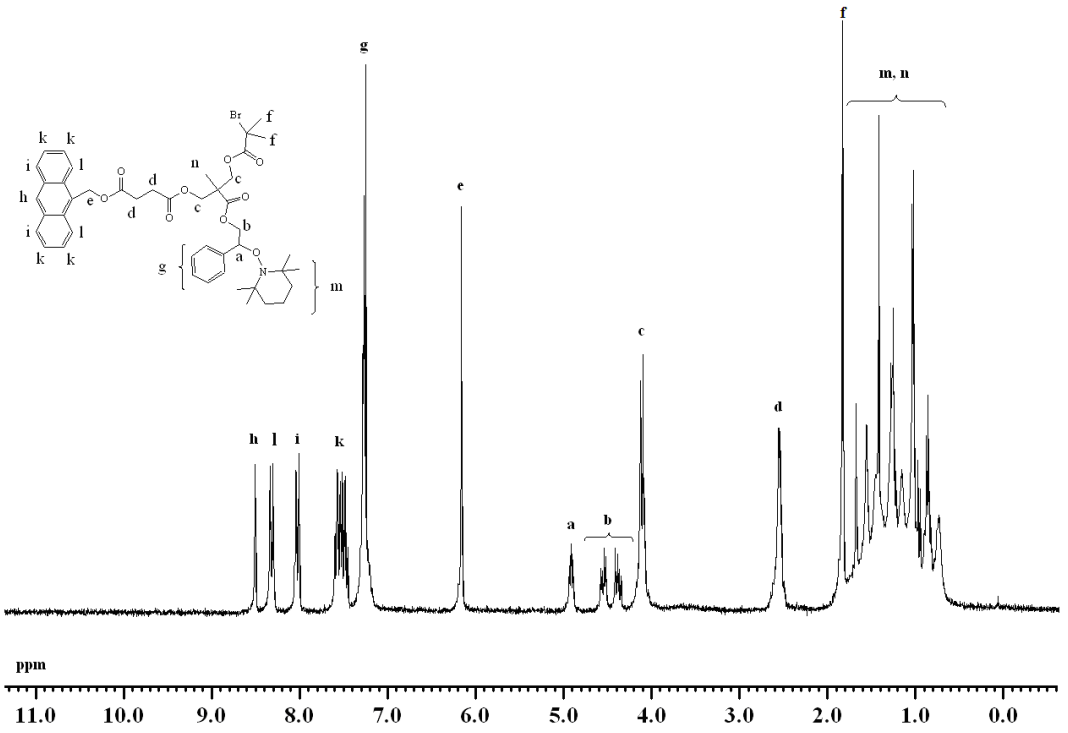
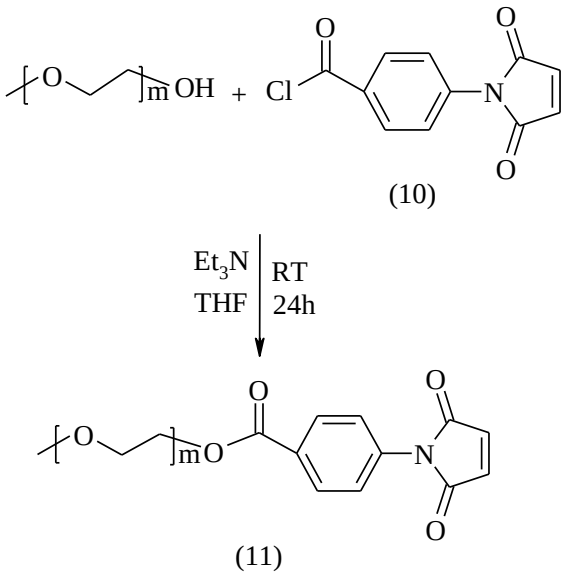




**Figure 4.8 :** The $^1$H NMR spectrum of succinic acid anthracen-9-ylmethyl ester 3-(2-bromo-2-methyl-propionyloxy)-2-methyl-2-[2-phenyl-2-(2,2,6,6-tetramethyl piperidin-1-yloxy)-ethoxy- carbonyl]-propyl ester in $CDCl_3$.

### 4.1.2. Esterification of PEG with 4-maleimido-benzoylchloride: [11]

4-maleimidobenzoyl chloride **(10)** was obtained according to a published procedure (yellow solid in 70% yield) [65]. PEG ($M_n$ = 550) was reacted with **(10)** in THF under nitrogen to give **11**, in 96% yield (Scheme 4.9). The $^1$H NMR spectrum of the compound**, (11)**, is shown in Figure (4.9).




(4.9)

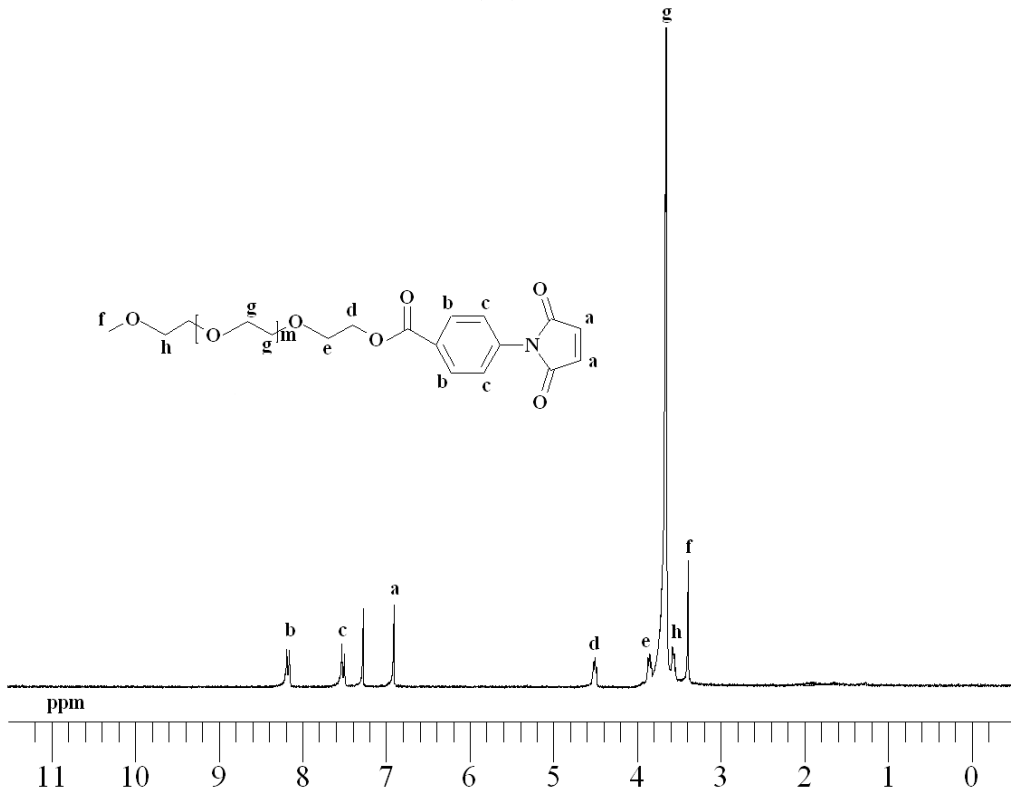
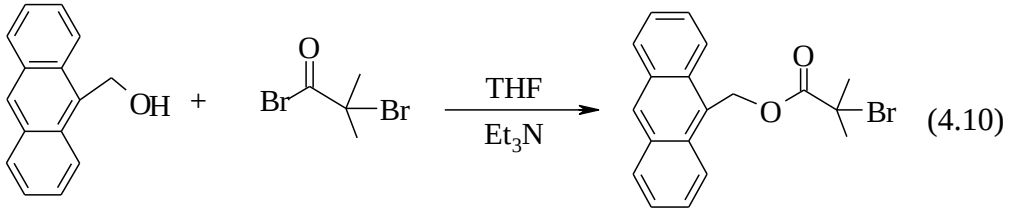



**Figure 4.9 :** The $^1$H NMR spectrum of PEG-maleimide **(11)** in $CDCl_3$.

### 4.1.3. Synthesis of 9-anthyrylmethyl 2-bromo-2-methyl propanoate [12]

9-anthyrylmethyl 2-bromo-2-methyl propanoate **(12)** was obtained according to a published procedure (yellow solid in 70% yield) [66]. The synthesis of 9-anthryl methyl 2-bromo-2-methyl propanoate is represented in scheme 4.10. The $^1$H NMR spectra of the compound, **(12)**, showed no signal corresponding to OH bond and this is an evidence for a good esterification reaction (Figure 4.10). According to the integration of $^1$H NMR ($CDCl_3$) spectrum of **12** : 7.43-8.52 (m, 9 Ar*H* of anthracene) 6.21 (s, 2H, C*H*$_2$-O), 1.87 (s, (C*H*$_3$)$_2$-C-Br).




(4.10)

12

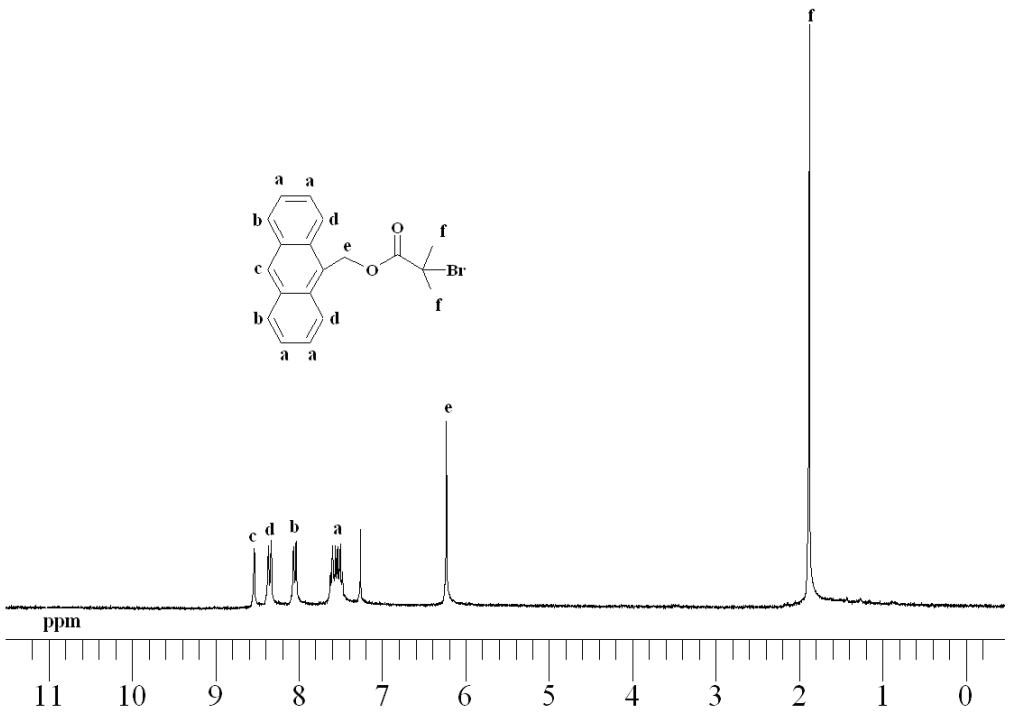



**Figure 4.10 :** The $^1$H NMR spectrum of 9-anthyrylmethyl 2-bromo-2-methyl propanoate **(12)** in $CDCl_3$.

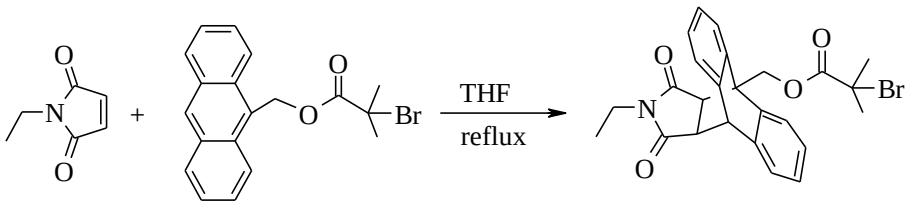
## 4.2. Model Diels-Alder Reactions

### 4.2.1. DA reaction between *N*-ethyl maleimide and 9-anthyrylmethyl 2-bromo-2-methyl propanoate (12): [13]

*N*-ethyl maleimide and **12** were refluxed in THF under nitrogen to give cyclo-adduct, 13, in 96% yield (Scheme 4.11).

The structure of **13** was confirmed by $^{1}$H NMR upon the assignment of a complete disappearance of anthracene singlet peak and maleimide ring protons at 8.5 and 6.65 ppm, respectively. Moreover, two new signals corresponding to a bridgehead proton of cyclo-adduct (C*H*) at 4.76 and two C*H* protons of the imide ring at 3.11-3.08 ppm were detected. The $^{1}$H NMR spectrum of the resulting compound, **(13),** is shown in Figure 4.11.

DA adduct formation is also monitored by UV spectrophotometer. Because, compound **12**, shows characteristic five-finger absorbance from 300 to 400 nm. However, **13** shows no remarkable peak in this region indicating a quantitative DA reaction. UV spectra of **12** and **13** is shown in Figure 4.12.




12 13 (4.11)

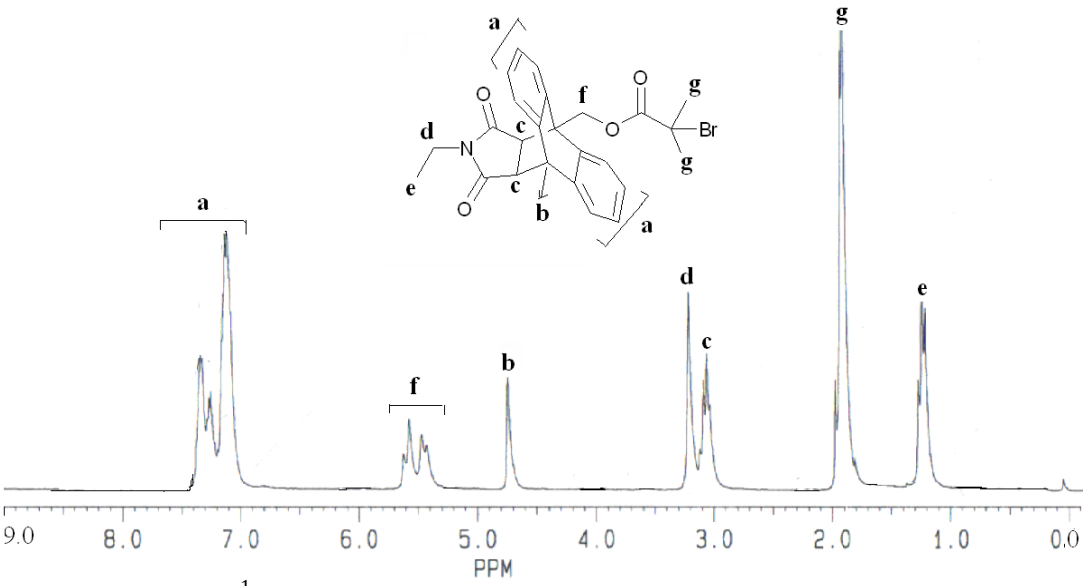



**Figure 4.11:** The $^{1}$H NMR spectrum of DA adduct between *N*-ethyl maleimide and 9-anthyrylmethyl 2-bromo-2-methyl propanoate **(12)** in $CDCl_3$.

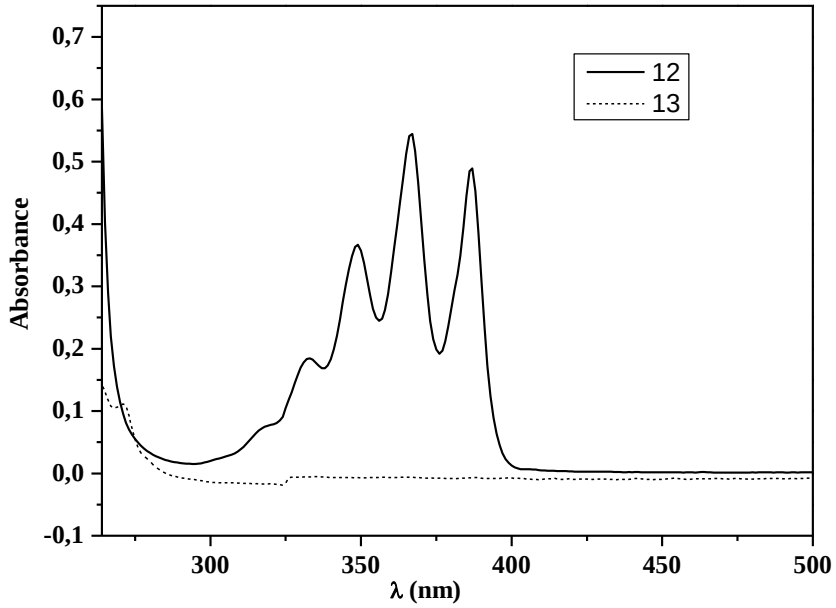
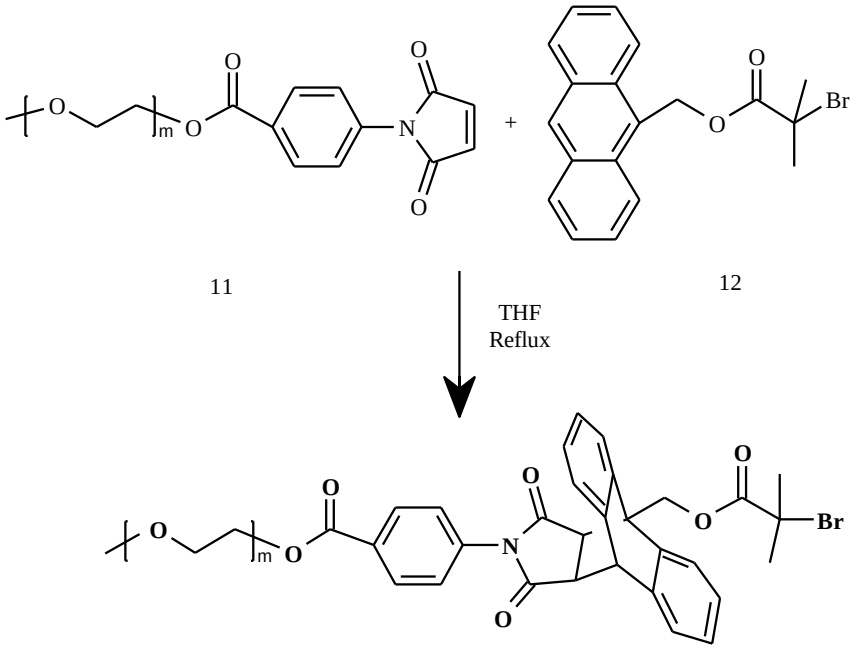



**Figure 4.12:** UV spectra of **(12)**: 5.36 X $10^{-5}$ M; and **(13)**: 5.1 X $10^{-5}$ M in $CH_2Cl_2$.

### 4.2.2. DA reaction between PEG-maleimide (11) and 9-anthyrylmethyl 2-bromo-2-methyl propanoate (12): [14]

DA adduct, **(14)**, was obtained from a reaction of PEG-maleimide, (**11**), with **12** at THF reflux temperature in 95% yield (Scheme 4.12). The structure of DA adduct **14** was confirmed by $^{1}$H NMR spectrum. A singlet peak of $CH_2$ protons (6.21 ppm) linked to anthracene group was shifted to 5.64 and 5.49 ppm as a doublet of doublet.

A characteristic singlet peak of maleimide CH=CH protons was shifted to upper field (3.54- 3.48 ppm). Moreover, a new signal corresponding to a bridgehead proton (CH), which resulted from a cyclo-addition reaction of maleimide and anthracene units was detected at 4.88 ppm as a singlet. $^{1}$H NMR spectrum of the desired compound, **(14),** is shown in Figure 4.13.




11 12 (4.12)

14

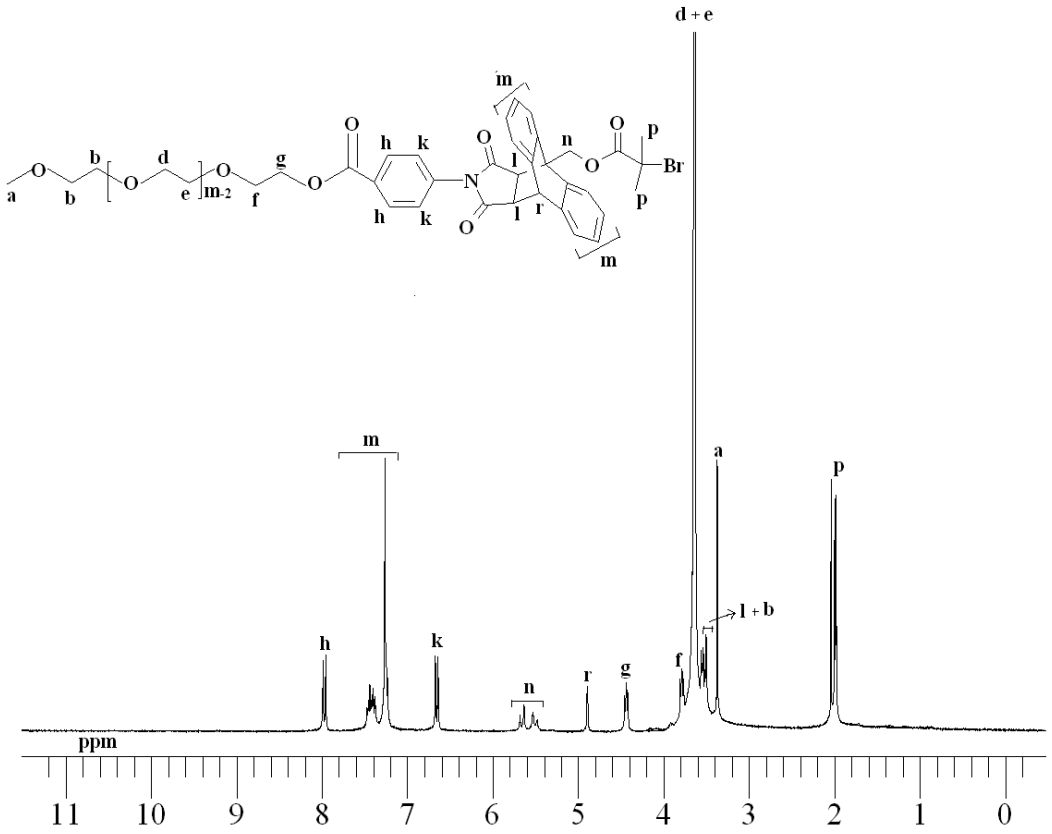



**Figure 4.13:** The $^{1}$H NMR spectrum of DA adduct between PEG-maleimide **(11)** and 9-anthyrylmethyl 2-bromo-2-methyl propanoate **(12)** in $CDCl_3$.

### 4.3. Preparation of PEG-PSt-P*t*BA Miktoarm Star Terpolymer

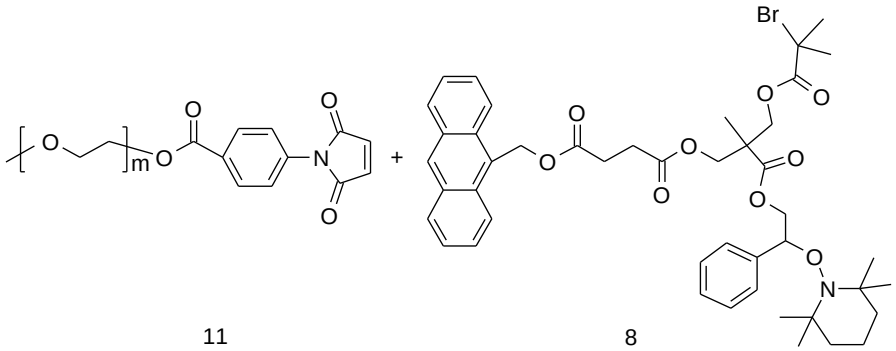
As stated previously, we aimed to prepare ABC type miktoarm star polymer using the miktofunctional initiator, (**8)**, via successive three step reactions involving DA reaction, SFRP and ATRP.

#### 4.3.1. DA reaction of PEG-maleimide (11) with the initiator (8): [15]

First PEG-maleimide, (**11)**, was allowed to react with **8** in order to give a PEG macroinitiator, (**15)**, with TEMPO and *tert*-bromide functional end groups (scheme 4.13). Thus, TEMPO and ATRP initiator (*tert*-bromide group) functionalities were quantitatively introduced into a PEG-macroinitiator **(15)**. From $^{1}$H NMR spectrum of **15**, a singlet peak at 8.51 ppm that was assigned as an anthracene aromatic proton, shifted to 4.86 ppm due to DA reaction between maleimide and anthracene groups. It also revealed that aromaticity of central phenyl unit of anthracene disappeared as a result of DA cyclo-addition reaction, and appeared a bridgehead proton as a new signal. The signals associated with TEMPO and *tert*-bromide functionalities are also

detected from 1.83 to 0.73 ppm. The $^{1}$H NMR spectrum of the compound, **(15)**, is shown in Figure 4.15.

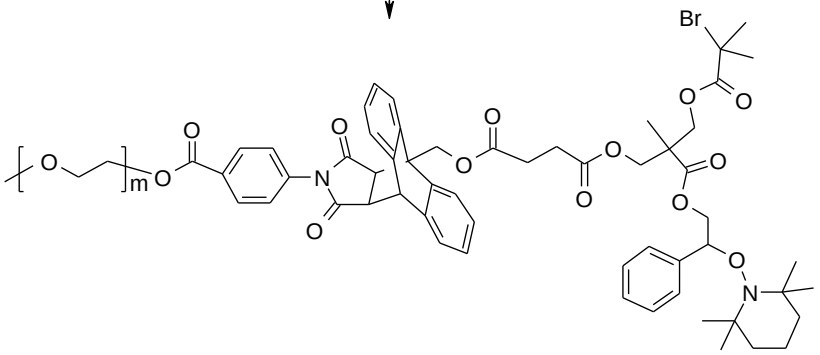
The NMR number-average molecular weight ($M_{n,NMR}$) of PEG-macronitiator, (**15)**, was calculated from a ratio of peak areas of PEG repeating unit around 3.60 ppm and $CBr(CH_3)_2$ of ATRP functional group around 1.83. To this value added was the molecular weight of **8**. DA reaction between **8** and **11** is also monitored by UV measurement (Figure 4.14). The characteristic absorbance of **8** in the range of 300-400 nm was completely disappeared upon a reaction with **11**, while giving **15**. On the other hand, PEG-maleimide, **(11)**, had no significant absorbance in this region.




11 8

(4.13)

THF
Reflux




15

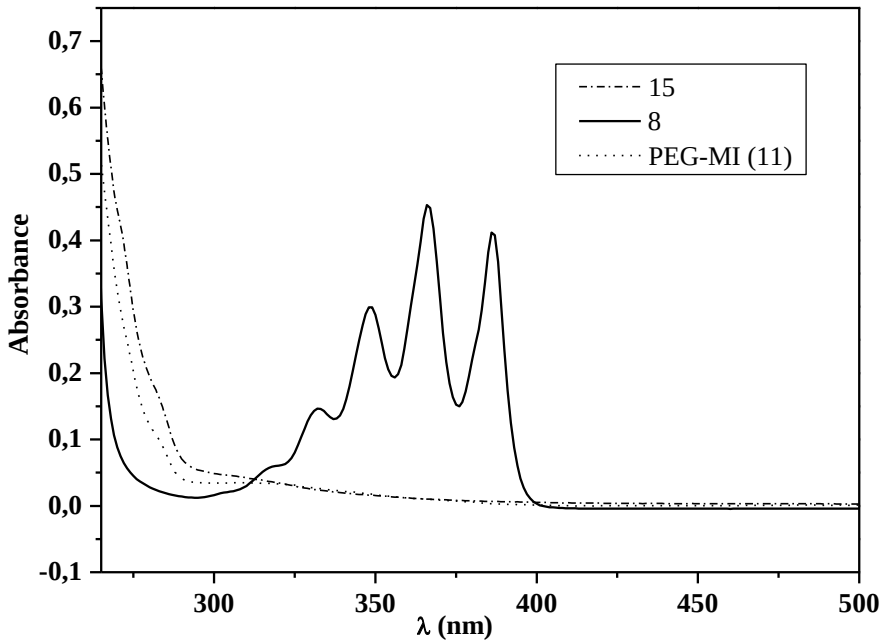



**Figure 4.14 :** UV spectra of PEG-MI **(11)**: 6.21 X $10^{-5}$ M; **8**: 6.9 X $10^{-5}$ M; and **15**: 6.58 X $10^{-5}$ M in $CH_2Cl_2$.

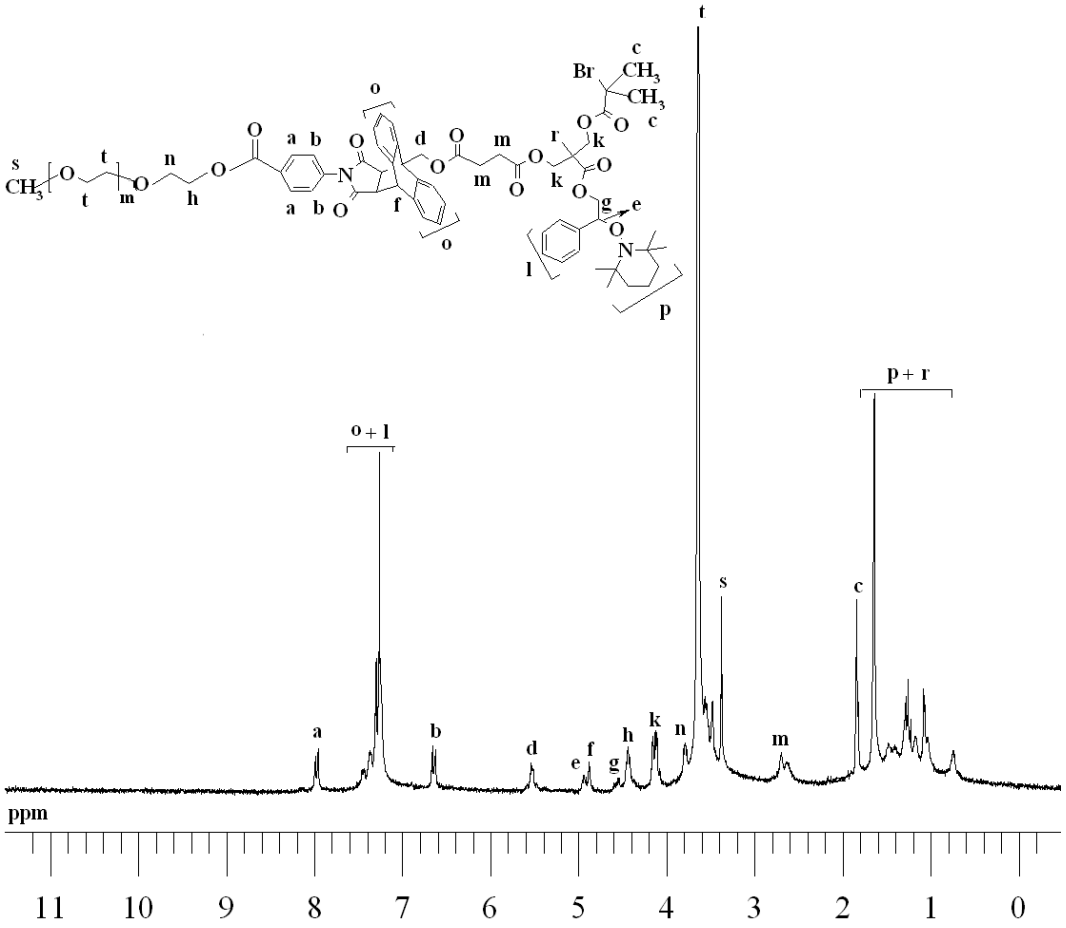
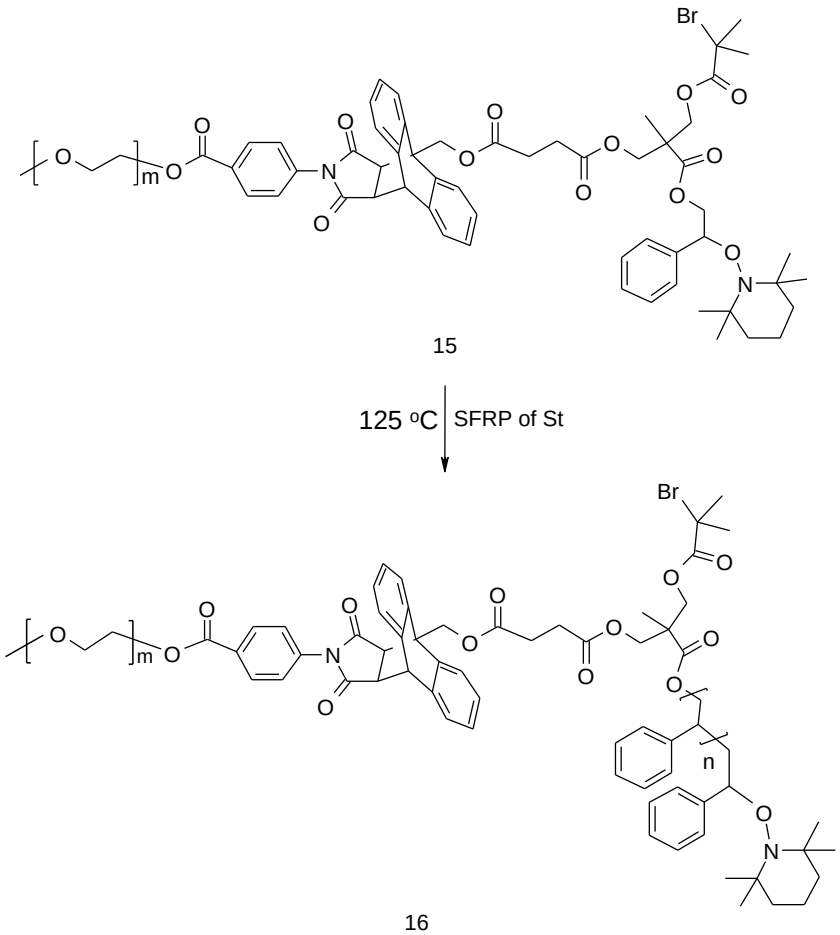



**Figure 4.15:** The $^1$H NMR spectrum of DA adduct of PEG-maleimide **(11)** with the initiator **(8)** in $CDCl_3$.

### 4.3.2. Preparation of PEG-PSt precursor (16) using PEG-macroinitiator (15) by SFRP of St: [16]

Previously obtained PEG-macroinitiator, (**15)**, was used as a macroinitiator for SFRP of St at 125 $^{o}$C. The signals of the aromatic group were assigned by means of $^{1}$H NMR confirming the incorporation of the St block into the PEG-PSt precursor, (**16)**. The theoretical number average molecular weight ($M_{n,theo}$) of PEG-PSt precursor was calculated by using following equation: $M_{n,theo}$ = ($[M]_o/[I]_o$) X conversion X 104 + $M_{n,NMR}$ of PEG precursor, (**15)**. $M_{n,NMR}$ of PEG-PSt block copolymer, determined from a ratio of integrated signals at 6.5-7.2 ppm to 3.89-3.52 ppm, was consistent with those of $M_{n,theo}$ and the number average molecular weight calculated by GPC ($M_{n,GPC}$).




(4.14)

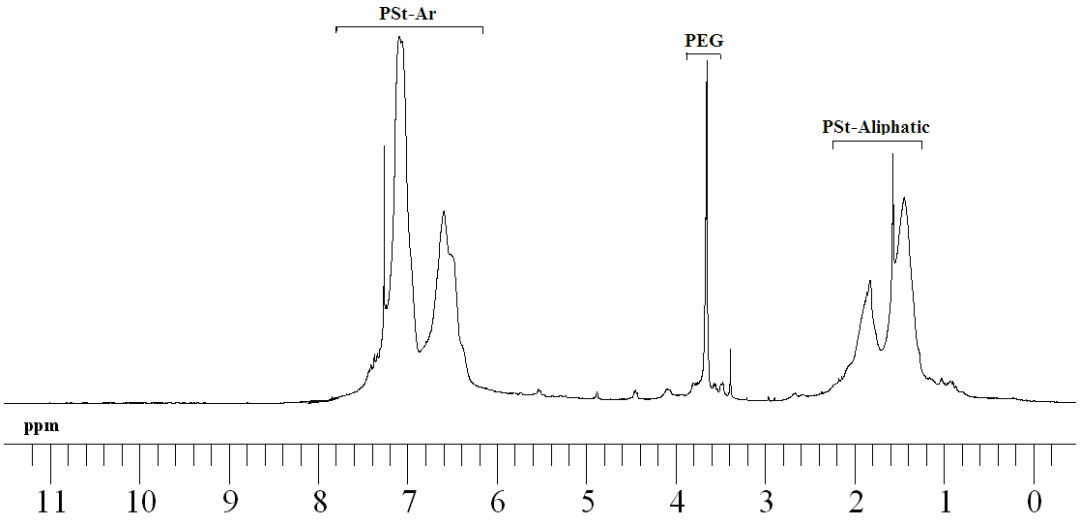
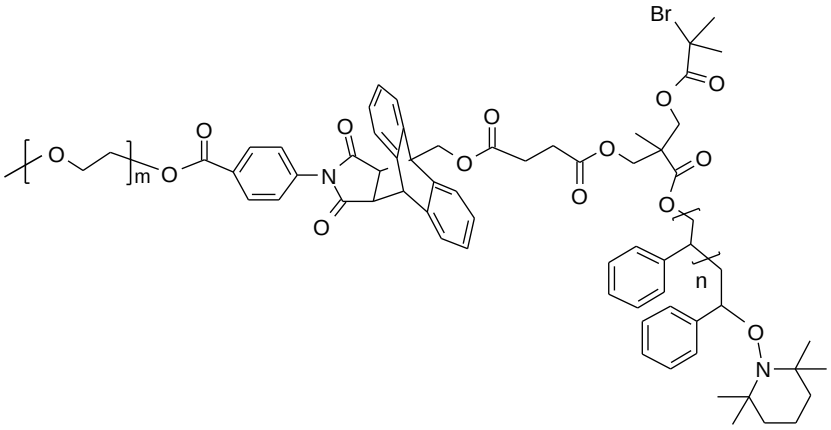



**Figure 4.16:** The $^{1}$H NMR spectrum of PEG-PSt macroinitiator in $CDCl_3$.

### 4.3.3. Preparation of PEG-PSt-P*t*BA miktoarm star terpolymer (17) by ATRP of *t*BA: [17]

As a third step, PEG-PSt precursor, (**16)**, consisting of an activated *tert*-bromide functionality was utilized as a macroinitiator for ATRP of *t*BA in the presence of CuBr/PMDETA complex system as a catalyst in bulk at 80 $^{o}$C. The signals centered at 1.4 ppm revealed the incorporation of P*t*BA arm affording ABC type miktoarm star polymer, **17a** and **b**, (Figure 4.17).

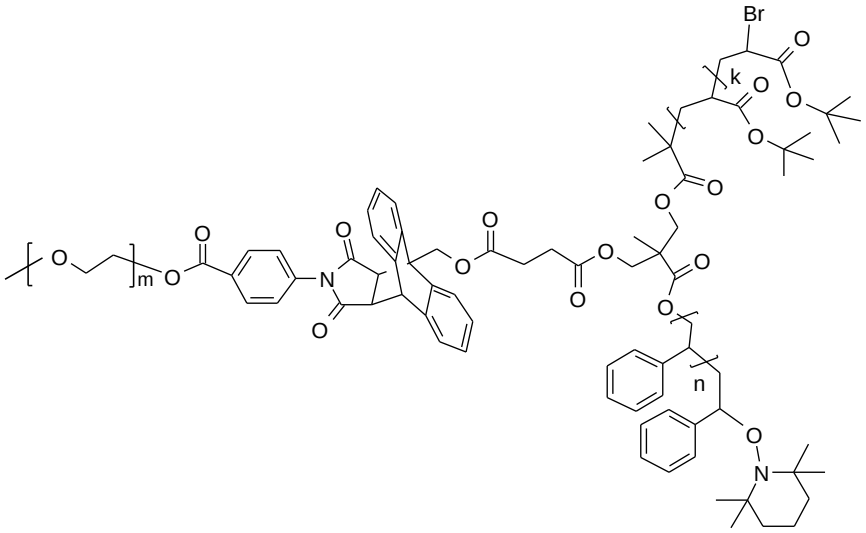
$M_{n,theo}$ of PEG-PSt-P*t*BA was calculated according to $M_{n,theo}$ = $([M]_o/[I]_o)$ X conversion X 128.17 + $M_{n,NMR}$ of PEG-PSt precursor, and the molecular weight of the resulting miktoarm star ($M_{n,NMR}$) was determined accordingly from the integration of the signals at 1.4, 3.63 and 6.5-7.2 ppm related to *tert*-butyl, $CH_2CH_2O$, and aromatic protons, respectively. The theoretical and NMR molecular weights are in good agreement. The conversions of ATRP process are particularly kept low due to probability of star-star coupling reaction.



16

80 °C | ATRP of tBA

(4.15)



17 (PEG-PSt-PtBA Miktoarm Star Terpolymer)

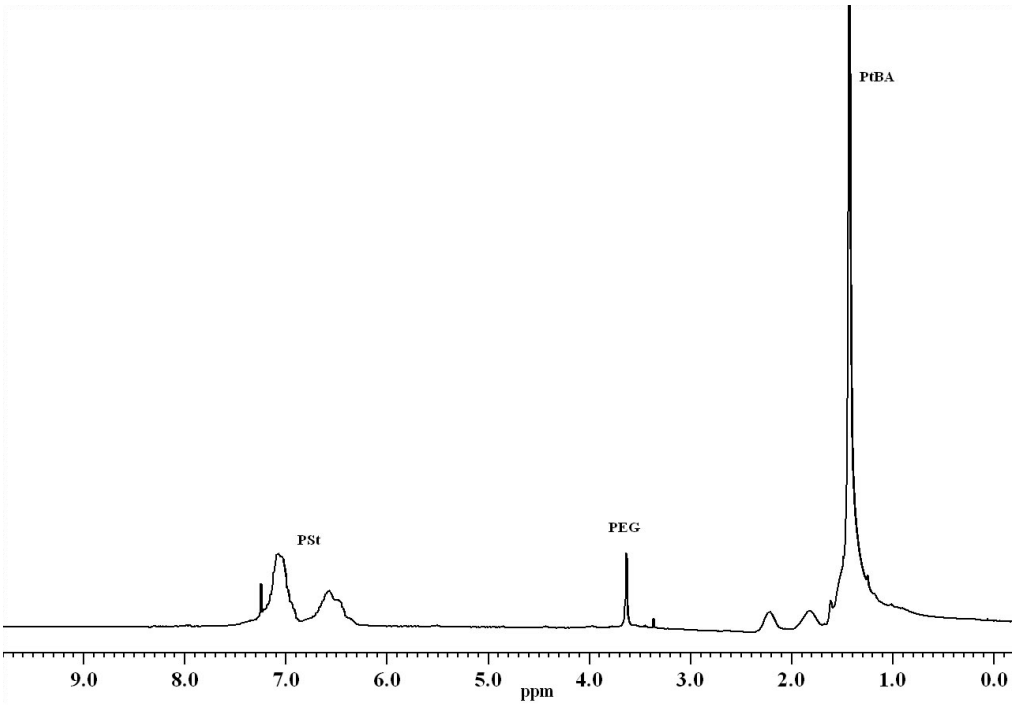



**Figure 4.17:** The $^{1}$H NMR spectrum of PEG-PSt-P*t*BA miktoarm star terpolymer **(17)** in $CDCl_3$.

The GPC traces of PEG-macroinitiator, (**15)**, PEG-PSt block, (**16)**, and PEG-PSt-P*t*BA miktoarm star terpolymer, (**17)**, are shown in Figure 4.18. The average molecular weight increased with styrene conversion in SFRP, confirming the introduction of the PSt block to the PEG precursor. Moreover, the disappearance of the PEG precursor peak revealed that the majority of the precursor chains having TEMPO moiety efficiently initiated the SFRP of St. A peak of the PEG-PSt block shifted to the higher molecular weight region with increasing monomer conversion in the ATRP of *t*BA. In addition, any peak in higher molecular weight region of the GPC traces was not observed indicating the absence of the star-star coupling reaction.

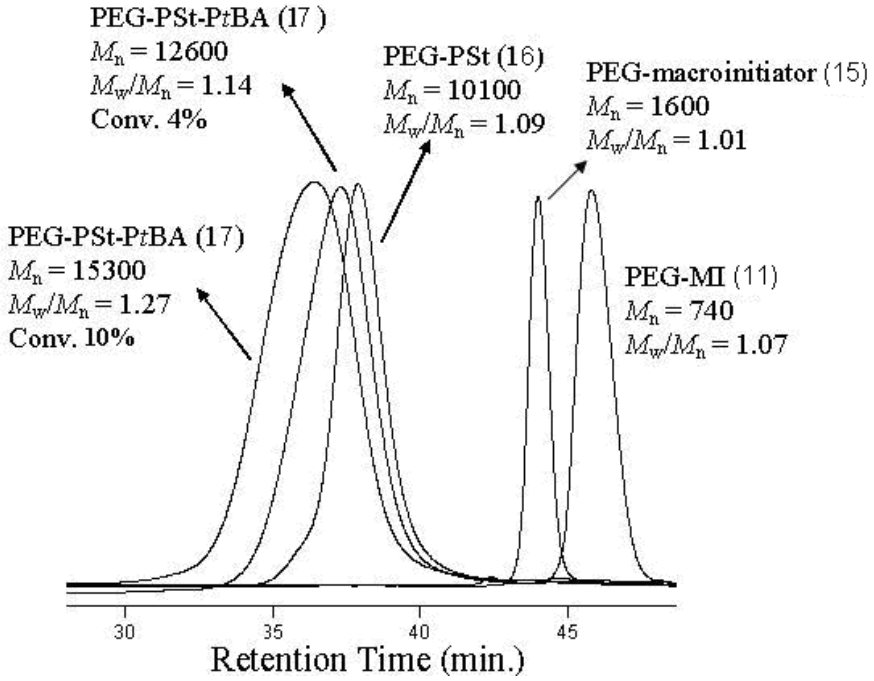



**Figure 4.18:** GPC traces of PEG-MI **(11)**, PEG-macroinitiator **(15)**, PEG-PSt precursor **(16)**, and PEG-PSt-P*t*BA miktoarm star terpolymer **(17)**.

The thermal behavior of the polymers was investigated by DSC measurements (Figure 4.19a and 4.19b). PEGmaleimide, (**11)**, displayed three transitions at -60.4, -27.5, and -5.5 $^{o}$C regarding the glass transition ($T_g$), the crystallization ($T_c$), and the melting ($T_m$) temperatures, respectively. On the other hand PEG-macroinitiator, (**15)**, exhibited a new glass transition at -18.8 $^{o}$C. Moreover, PEG-PSt precursor, (**16)**, displayed a glass transition at 82.8 $^{o}$C, which was consistent with that of PSt homopolymer. Any $T_g$ regarding with PEG segment was not observed, due to the relatively shorter PEG compared with PSt segment. Additionally, for PEG-PSt-P*t*BA miktoarm star terpolymer, (**17)**, two $T_g$s at 45.9 and 83.9 $^{o}$C were observed. The first transition was almost identical to that of P*t*BA segment, while the second transition was similar to that of PSt segment.

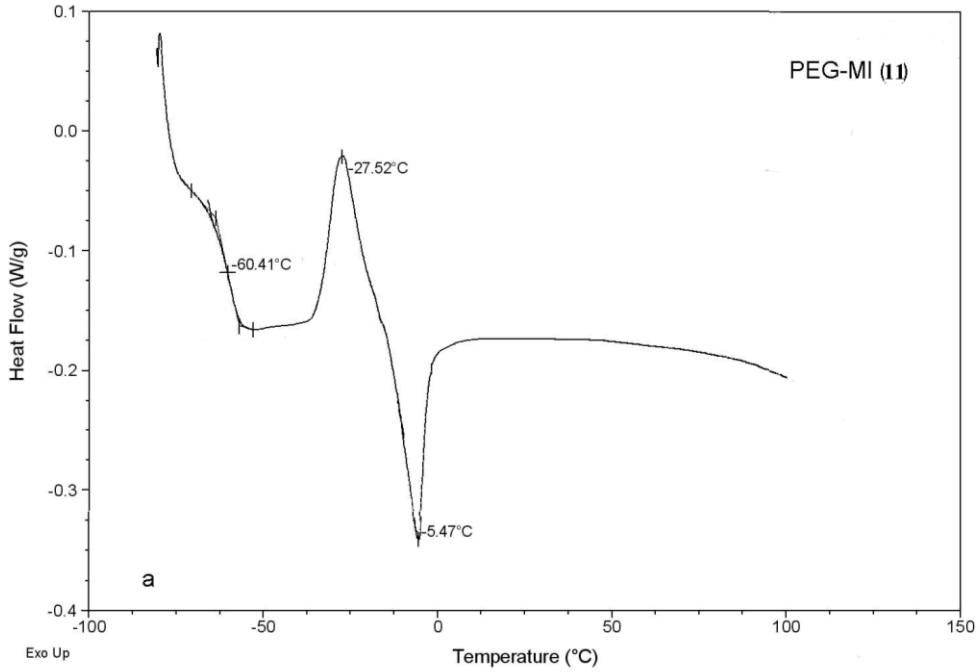



**Figure 4.19a :** DSC thermogram of PEG-MI **(11)**,

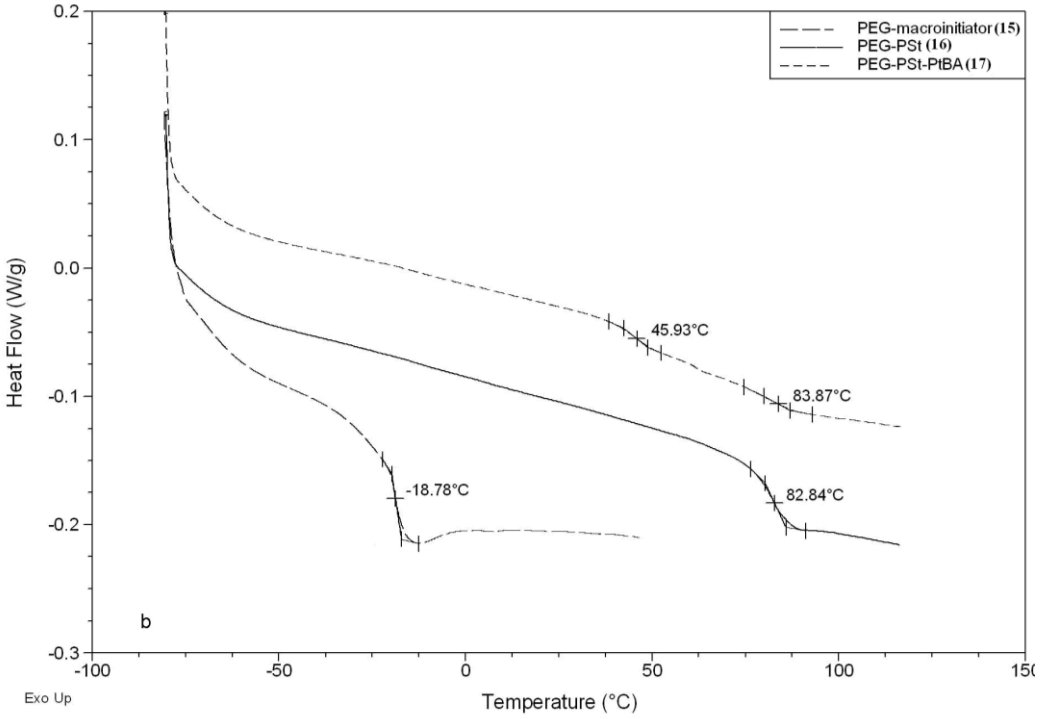



**Figure 4.19b :** DSC thermograms of PEG-macroinitiator **(15)**, PEG-PSt precursor **(16)**, and PEG-PSt-P*t*BA miktoarm star terpolymer **(17)**.

**Table 4.1:** Characteristics of PEG-PSt precursor **(16)** and PEG-PSt-P*t*BA miktoarm star terpolymer **(17)**.

| Entry | Monomer | $[M]_o$ (mol $L^{-1}$) | $[M]_o/[I]_o$ | Initiator | Time (min.) | Conv. (%) | $M_{n,theo}$ | $M_{n,NMR}$ | $M_{n,GPC}$ | $M_w/M_n$ [c] | DSC $T_g$ /$T_m$ ($^oC$) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| PEG-PSt (16)[a] | St | 8.73 | 100 | 15 | 900 | 85 | 10450 | 10900 | 10100 | 1.09 | $T_g$ = 82.8 |
| PEG-PSt-P*t*BA (17)[b] | *t*BA | 6.83 | 500 | 16 | 240 | 4 | 13600 | 14000 | 12600 | 1.14 | $T_g$ = 45.9<br>$T_g$ = 83.9 |
| PEG-PSt-P*t*BA (17)[b] | *t*BA | 6.83 | 500 | 16 | 360 | 10 | 17300 | 18500 | 15300 | 1.27 | - |

[a]Polymerization was carried out at 125$^o$C.

[b]$[I]_o$: $[PMDETA]_o$: $[CuBr]_o$ = 1:1:1; polymerization was carried out at 80 $^o$C.

[c] Calculated from GPC calibrated with linear polystyrene standards.

## 5. CONCLUSION

Miktofunctional initiator, **(8)**, possessing anthracene, TEMPO and ATRP initiator functionalities was synthesized and employed in successive DA reaction and controlled radical polymerization routes, e.g. SFRP and ATRP in order to give ABC type miktoarm star terpolymer containing PEG, PSt and P*t*BA arms. We here used "core in" and "core out" processes jointly for the synthesis of ABC type miktoarm star polymer. In a "core in"process, DA reaction between PEG-maleimide and anthracene functionalized initiator, **(8)**, was carried out quantitatively to give PEG-macroinitiator, **(15)**. This macroinitiator was then used in subsequent SFRP and ATRP routes (core out processes). DA reaction as a "core in" process may afford a new synthetic approach for the preparation of miktoarm star polymer.

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